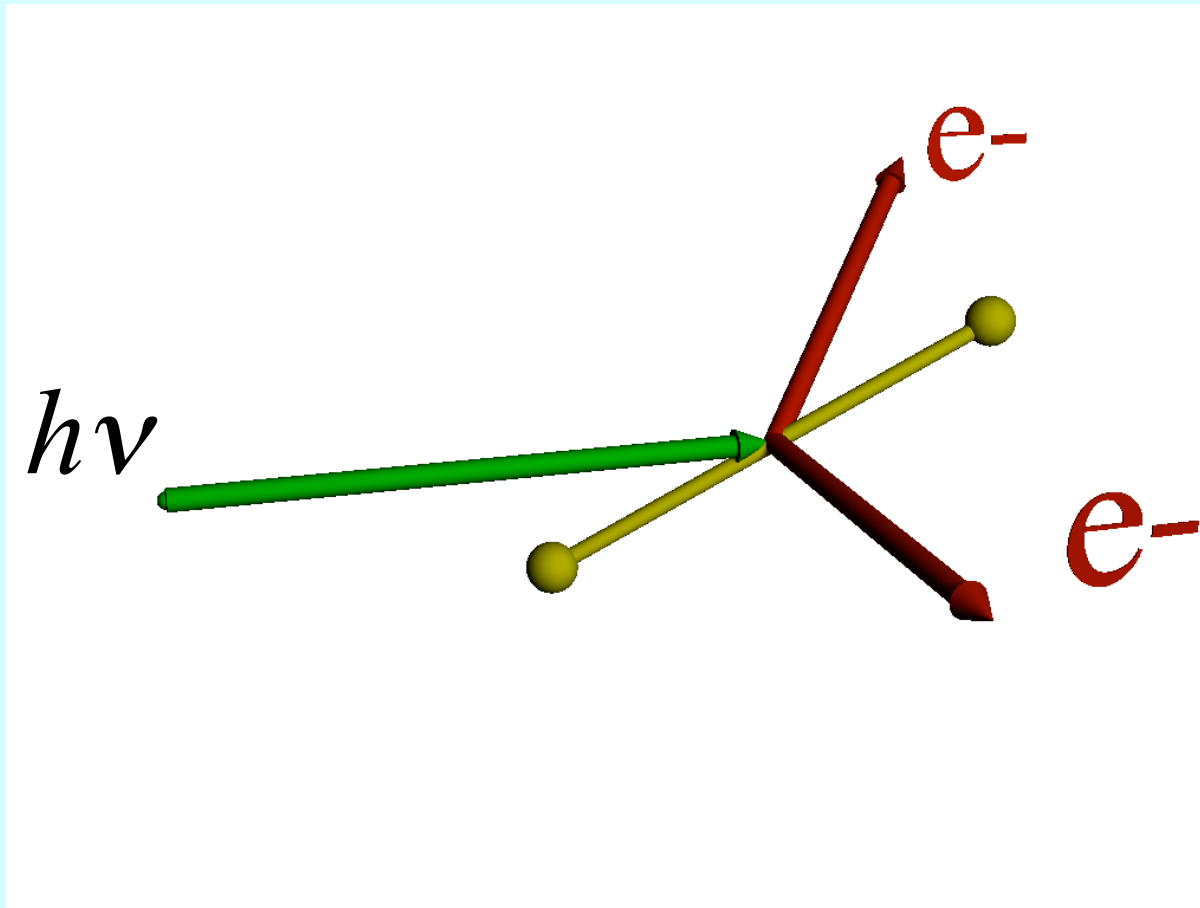


Using Advanced Computation to Solve the Coulomb Breakup Problem

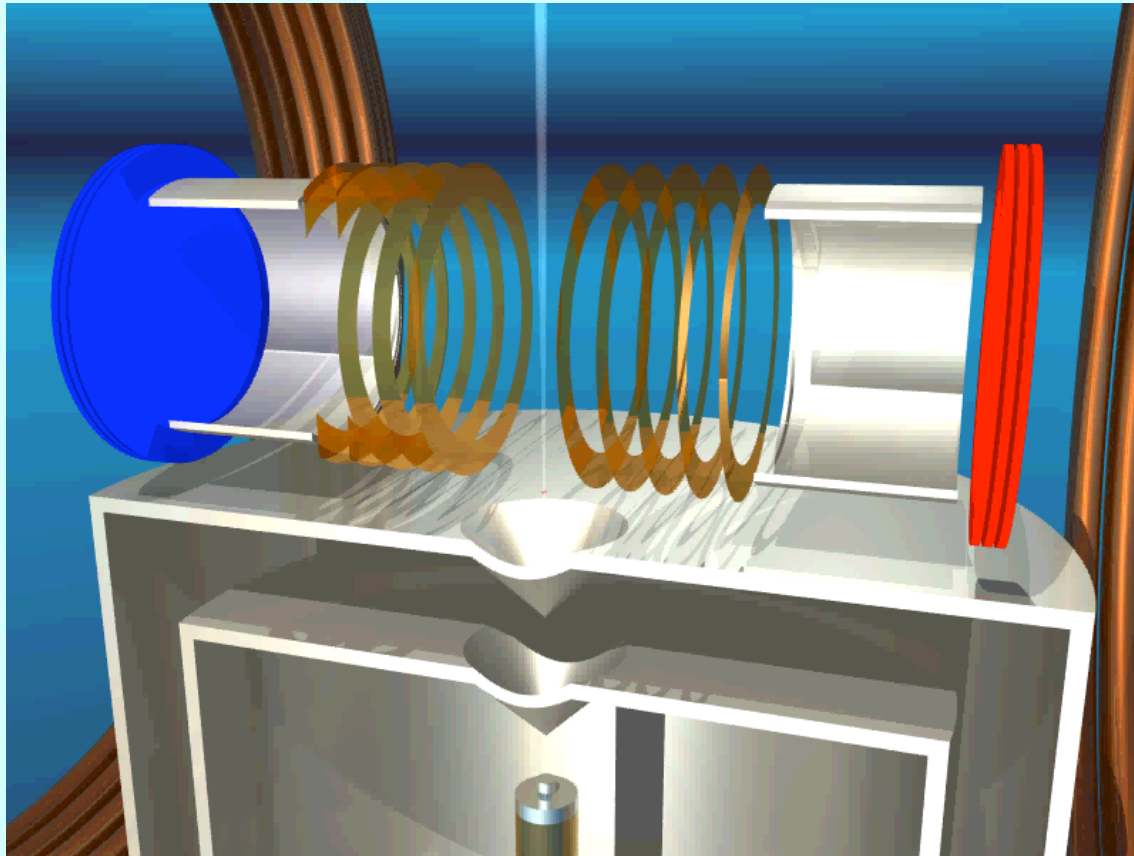
C. William McCurdy, U. C. Davis
and the Lawrence Berkeley National Lab



Imagine a Perfect Photofragmentation Experiment



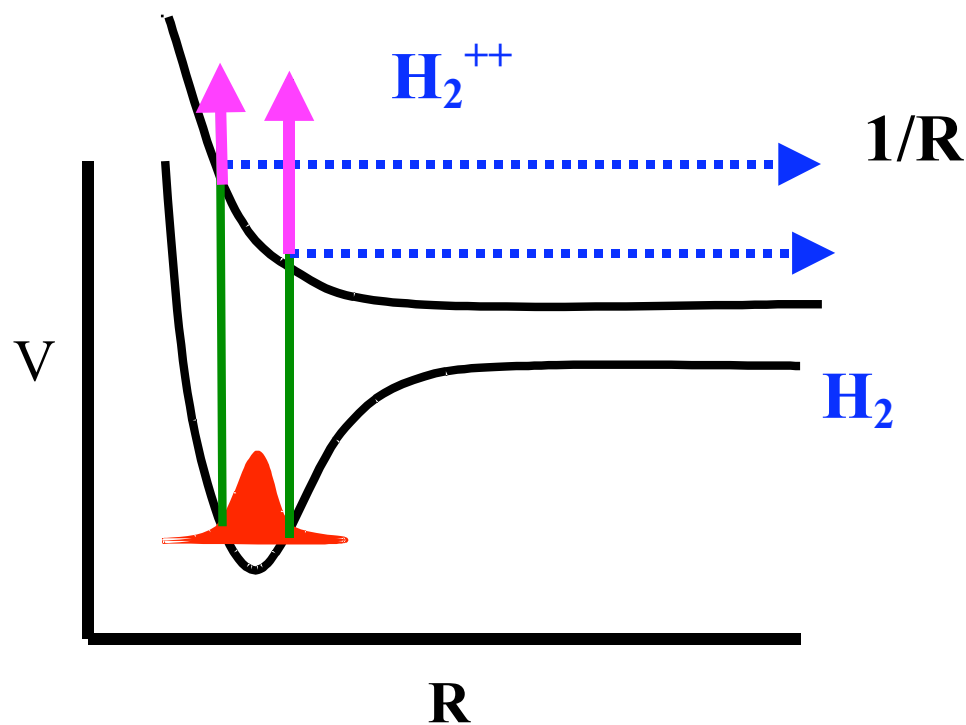
Catching all the charged particles in coincidence -- The COLTRIMS method



(Frankfurt group)

- **Measurement of the directions and velocities of all the charged particles that come from a given event**
- **Data can be collected for hundreds of thousands of events**
- **Soft X-ray photons from the Advanced Light Source at LBNL**

We Can Even Measure the Internuclear Distance at Which the Ionization Occured



(Assuming the Born-Oppenheimer Approximation)

Why Are These Problems Interesting?

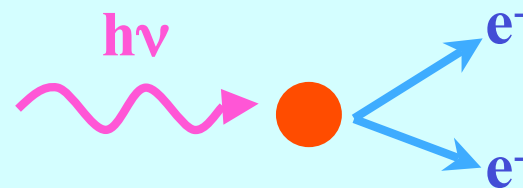
Breakup Leading to Two or More Unbound Electrons:

1. Double Photoionization of atoms and molecules
2. Electron-Impact Ionization

- How does double photoionization probe electron correlation in the target?
- How are the motions of two or more electrons correlated in ionization processes that result in more than one electron leaving an atom or molecule?

In the absence of correlation there would be essentially no cross section -- e.g., He:

$$\langle \varphi_{1s}(1)\varphi_{1s}(1) | \varepsilon \cdot r_1 + \varepsilon \cdot r_2 | \varphi_{ks}(1)\varphi_{kp}(2) \rangle \approx 0$$

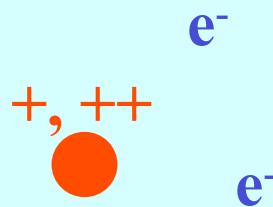


Why Are These Problems Difficult?

- Double photoionization of atoms and molecules and electron-impact ionization are processes that place two electrons “in the continuum”



- The final state contains three separating charged particles



Why was this few-body problem not “reduced to computation” –*even in principle* – until the late 1990’s?

The Nature of Scattering Problems



Map *known* “incoming” solutions onto *known* “outgoing” solutions

$$\Psi_{\text{in}} \Rightarrow \Psi_{\text{interacting}} \Rightarrow \Psi_{\text{out}}$$


Boundary conditions (e.g. one particle)

$$\Psi \rightarrow \underset{\text{in}}{e^{i\mathbf{k}\cdot\mathbf{r}}} + \underset{\text{out}}{f(\vartheta, \varphi) e^{ikr} / r}$$



Long Range Potentials: “Coulomb potentials are forever”

If the potential is $V \sim 1/r$:

- In classical mechanics, Kepler orbits, arbitrarily long elliptical orbits with a vector constant of motion along their major axis (Runge-Lenz vector) 
- In quantum mechanics, Coulomb boundary conditions, with logarithmic phases for electron-ion scattering and single photoionization.

$$\Psi \rightarrow e^{i\mathbf{k} \cdot \mathbf{r} + i\eta \ln(kr - \mathbf{k} \cdot \mathbf{r})} + f(\vartheta, \varphi) e^{i(kr - \eta \ln 2kr)} / r$$

logarithmic phases

The Formal Theory of Coulomb Three-Body Breakup

The asymptotic form of the wave function for 3-body Coulomb breakup was first given by Peterkop (1962) and Rudge and Seaton (1965)

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) \rightarrow -f(\hat{r}_1, \hat{r}_1, \alpha) i^{1/2} \left(K^3 / \rho^5 \right)^{1/2} e^{i \left(K\rho + \frac{\xi(\hat{r}_1, \hat{r}_1, \alpha)}{K} \ln(2K\rho) \right)}$$

where hyperradius $\rho = \sqrt{r_1^2 + r_2^2}$ and hyperradius $\alpha = \tan^{-1}(r_2 / r_1)$
 $K = \sqrt{2E}$ and $\xi(\hat{r}_1, \hat{r}_2, \alpha) = 1 / \sin(\alpha) + 1 / \cos(\alpha) - (1 - \cos(\vartheta_{12}) \sin(2\alpha))^{1/2}$

$f(\hat{r}_1, \hat{r}_1, \alpha)$ is the breakup amplitude

Matching to this form has proved computationally impractical to date, *because the logarithmic phase depends on the dynamical angles and is not separable in spherical coordinates!*

How To Get Around These Intrinsic Difficulties?

- First we need to reformulate the problem so that we can apply the right boundary conditions – somehow
- We need to find a way to computationally implement the solution so that we can “reduce the problem to computation” so that we can solve it to arbitrary accuracy
 - Bigger computer → more accuracy
- A good hint was lying around for decades, unnoticed in the context of breakup problems.

The Original Complex Scaling Idea

Early theorems: Aguilar, Balslev, Combes, and Simon 1970s

Early computations: Doolen, Nuttall, Reinhardt, ... 1970s

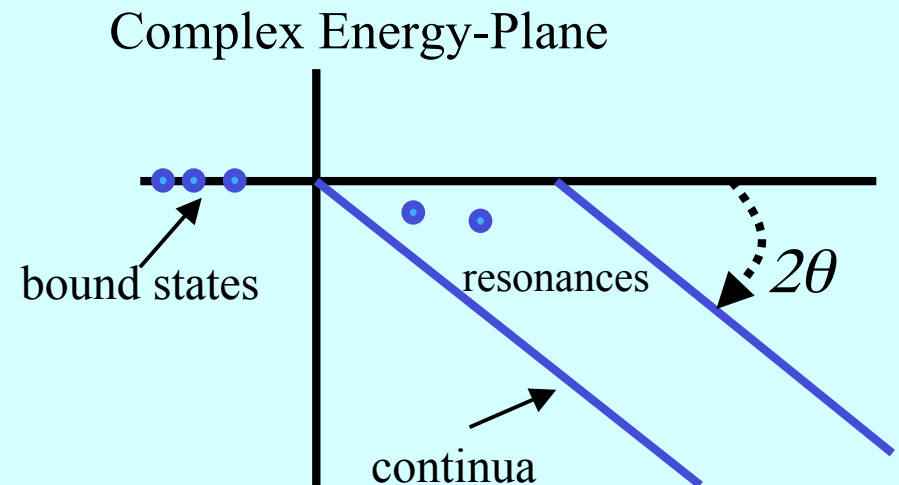
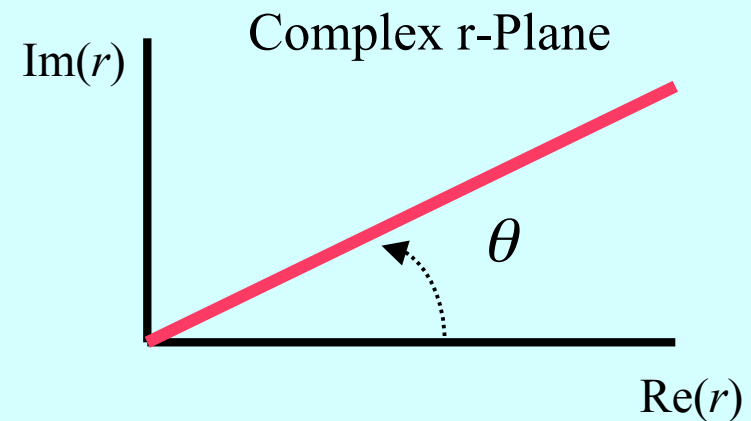
Scale all the radial coordinates of all the electrons by
 $r \rightarrow re^{i\vartheta}$

$$H_{\vartheta} = H(r_1 e^{i\vartheta}, r_2 e^{i\vartheta}, \dots)$$

The energy spectrum of the now non-Hermitian Hamiltonian changes. But resonance wave functions become square integrable $\Psi_{res}(re^{i\vartheta}) \xrightarrow{r \rightarrow \infty} 0$

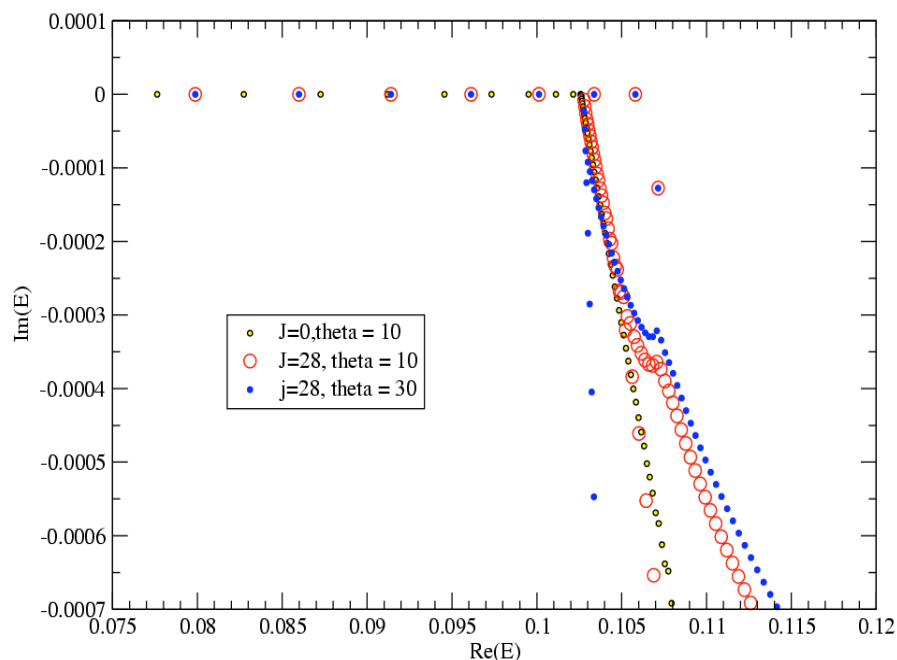
Program was to diagonalize H_{ϑ} in a basis and find the resonance energies and widths

$$E_{res} = E_R - i\Gamma / 2$$



$$H_{\vartheta} = e^{-2i\vartheta} T + e^{-i\vartheta} V$$

Example: Morse Oscillator with a Centrifugal Barrier ($J \neq 0$)



Calculation with B-spline basis, no dependence of resonance energies on scaling angle

The Hint: We can't use the discretized energy spectrum to compute the complete scattering Green's function when the coordinates are real and the discrete eigenvalues are real – *but we can when they are complex!*

$$\frac{1}{E - H + i\varepsilon} \approx \sum_n |\phi_n\rangle \frac{1}{\underbrace{E - E_n}_{\text{Need this at real } E}} \langle \phi_n |$$

Reformulating the Problem

Rearrange the Schrödinger equation so that we are always solving a *driven equation* which requires *pure outgoing boundary conditions* for $\Phi^{(+)}$

$$\Psi = \Phi^{(+)} + e^{ik \cdot r_2} \Psi_0(r_1)$$

Electron impact ionization: driven by the incoming wave

$$(E - H) \Phi^{(+)} = (H - E) A e^{ik \cdot r_2} \Psi_0(\mathbf{r}_1)$$

For double photoionization: driven by the dipole interaction

$$(E_0 + \hbar\omega - H) \Phi^{(+)} = \vec{\varepsilon} \cdot \vec{\mu} \Psi_0(\mathbf{r}_1, \mathbf{r}_2)$$

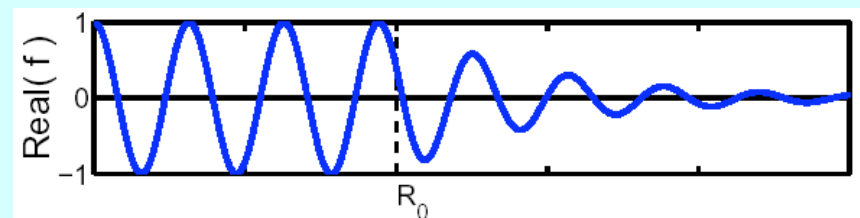
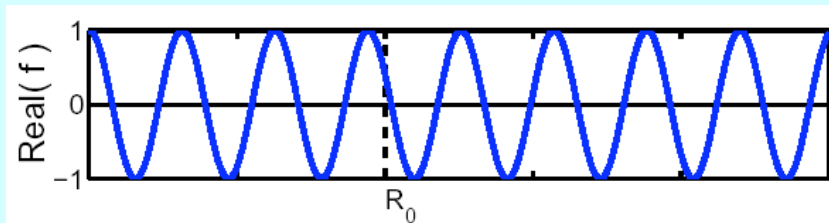
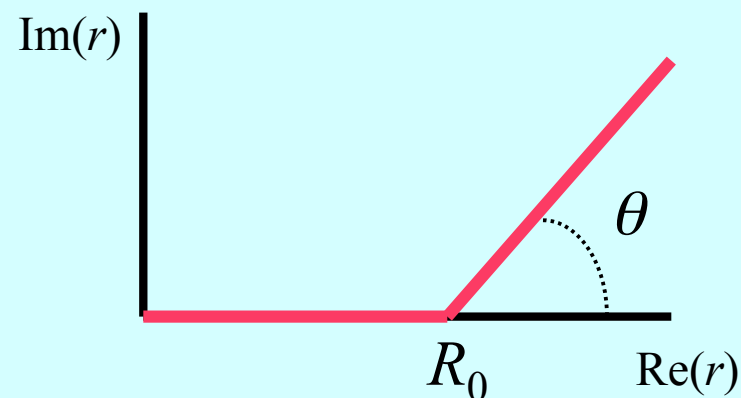
In both cases we need a purely outgoing solution:

$$\Phi^{(+)} = (E - H + i\varepsilon)^{-1} \chi(\mathbf{r}_1, \mathbf{r}_2)$$

The Key Idea: *Exterior Complex Scaling*

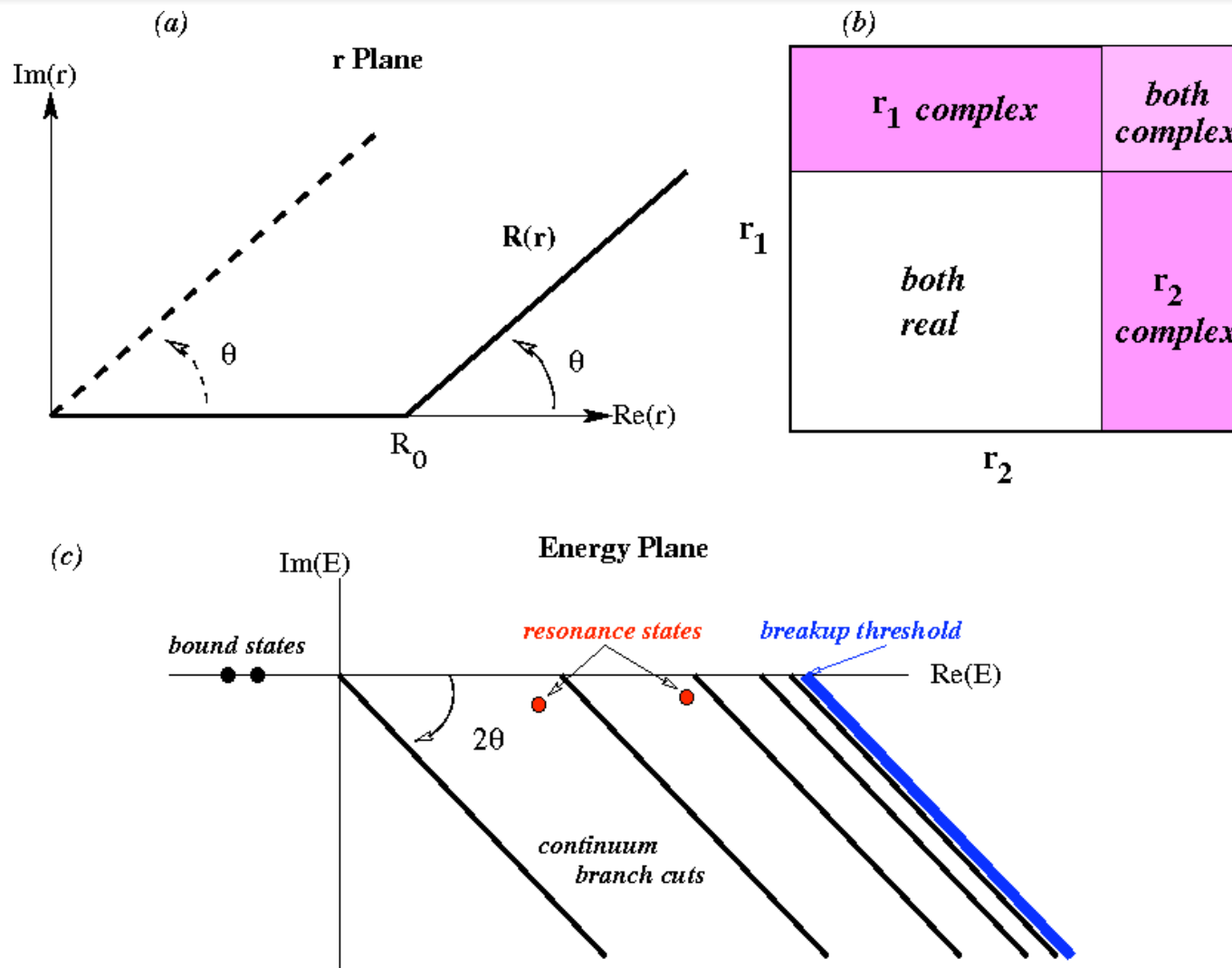
Exterior Complex Scaling (ECS) of the *radial* coordinates of both electrons applies the $\pm i\epsilon$ boundary condition and produces pure outgoing waves

$$R(r) = \begin{cases} r, & r \leq R_0 \\ (r - R_0)e^{i\theta}, & r > R_0 \end{cases}$$



Under ECS, outgoing waves, like e^{ikr} , are exponentially damped and the asymptotic boundary conditions are simplified.

Exterior Complex Scaling LEAVES THE WAVE FUNCTION UNCHANGED FOR $r < R_0$

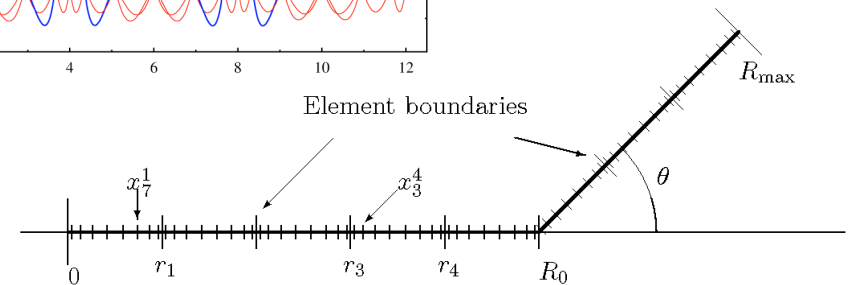
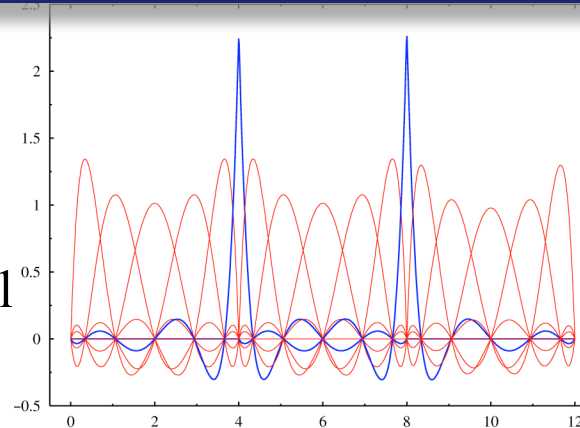
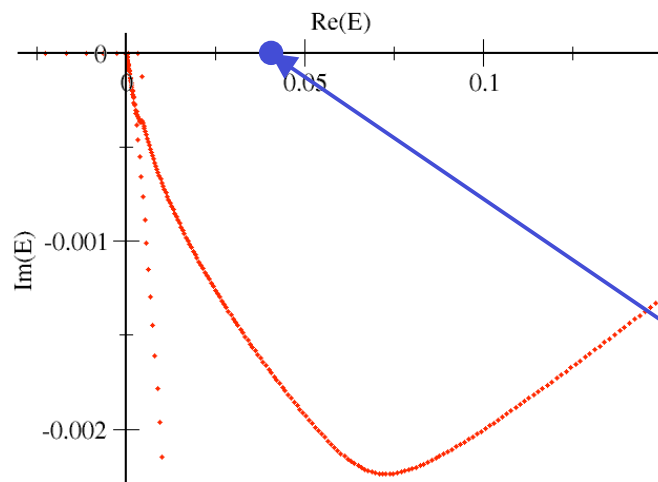


A Variety of Representations of ECS

- Finite Difference
- Finite Elements with Discrete Variable Representation (FEM-DVR) -- quadrature-based spectral representation
- B-splines

=> Large Sets of Linear Equations

Energy plane



(Automatically treats d/dr correctly at R_0)

$$\frac{d}{dr} \tilde{\Phi}^{(+)}(r) = \frac{dR(r)}{dr} \Phi^{(+)}(R(r))$$

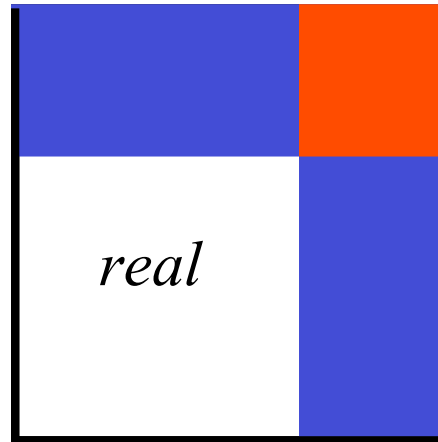
Continuous spectrum moves off the real axis allowing the evaluation of $(\mathbf{E} - \mathbf{H} + i\epsilon)^{-1}$ at real \mathbf{E} in a discrete basis

Exterior Scaling in Two Radial Dimensions

Apply Exterior
Scaling to both
radial coordinates

r_2 complex

r_2



both complex

r_1 complex

For $e^- + H$

$R_0 = 100 \text{ a}_0$

$r_{\max} = 150 \text{ a}_0$

r_1

Expand the scattered wave function in
(coupled) spherical harmonics

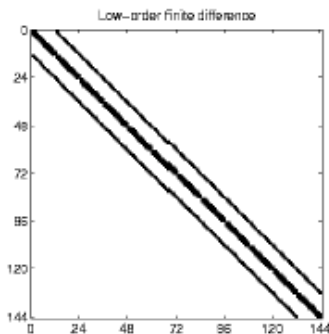
**Example: finite difference
with ~ 458 points in each
dimension \Rightarrow**

$$\Phi^+ = \sum_{L, l_1, l_2} \frac{\psi_{l_1, l_2}^L(r_1, r_2)}{r_1 r_2} Y_{l_1, l_2}^L(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2)$$

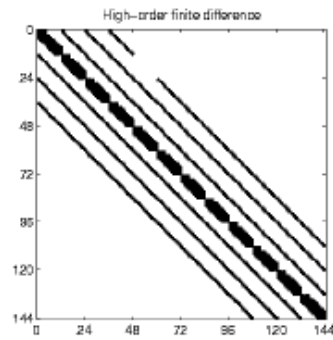
- Each $l_1 l_2$ block 209,764 x 209,764
- 24 coupled $l_1 l_2$ blocks gives **sparse system of order 5,034,336**

Modern Numerical Linear Algebra Algorithms Make it Possible

Precondition

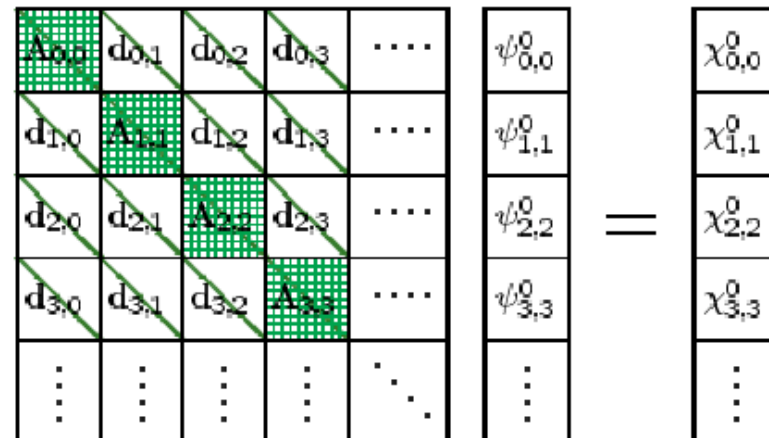


SuperLU -- **direct**
sparse solver, low-
order finite differ-
ence, uncoupled
blocks



Congugate Gradient,
high-order finite dif-
ference

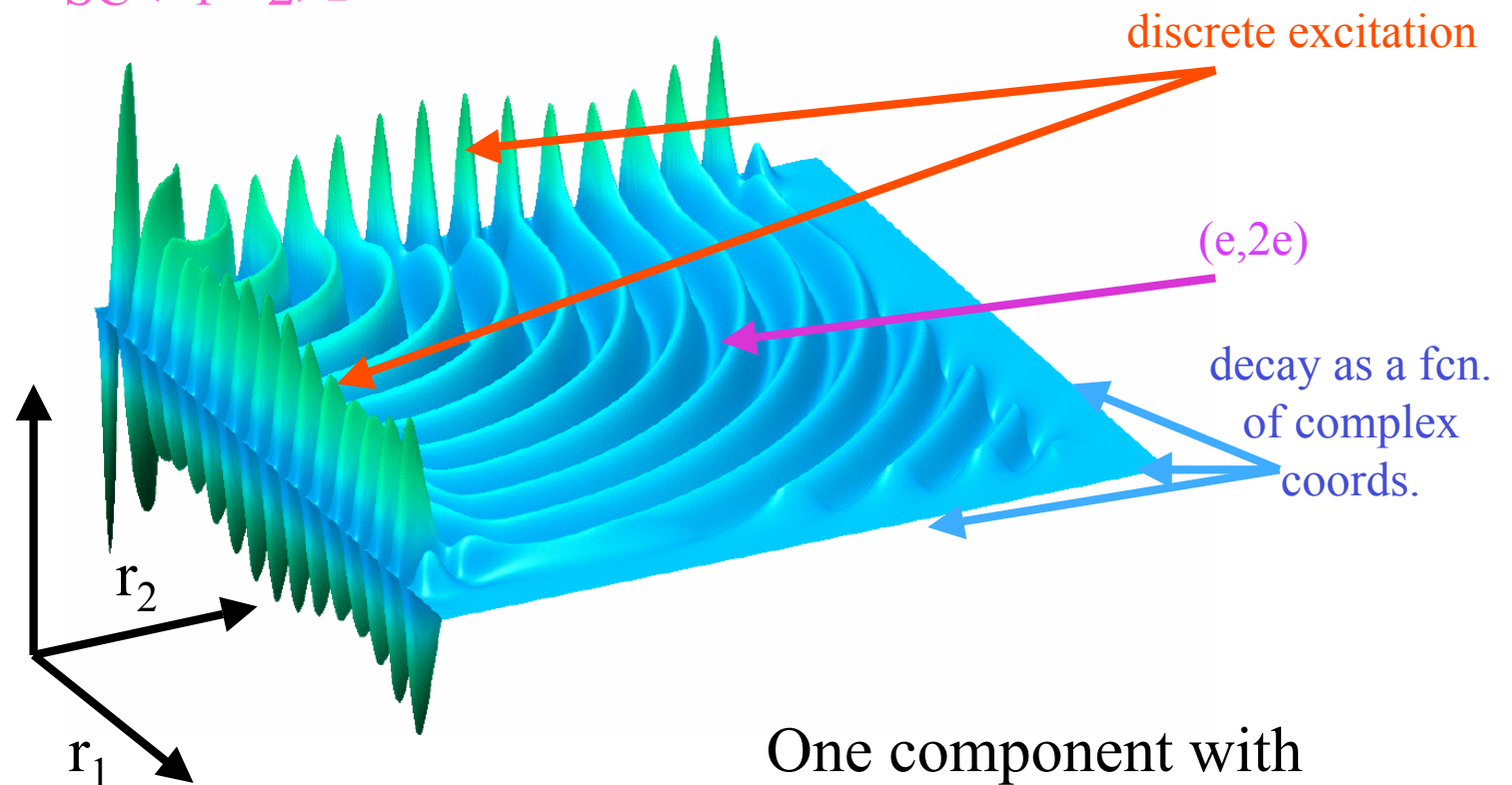
Precondition



Congugate Gradient,
full equations with
coupled $l_1 l_2$ blocks

The correct wave function decays to zero on the complex part of the contour, but contains all the physics for $r < R_0$

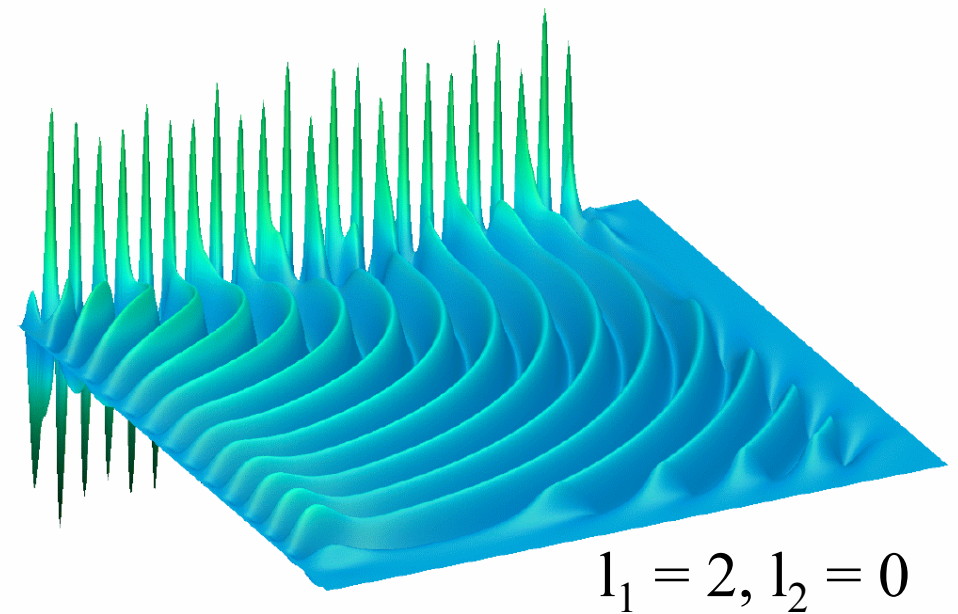
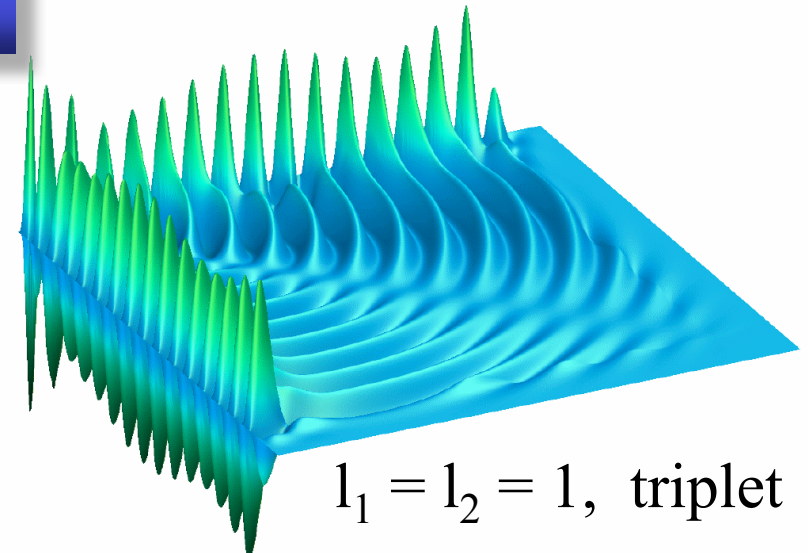
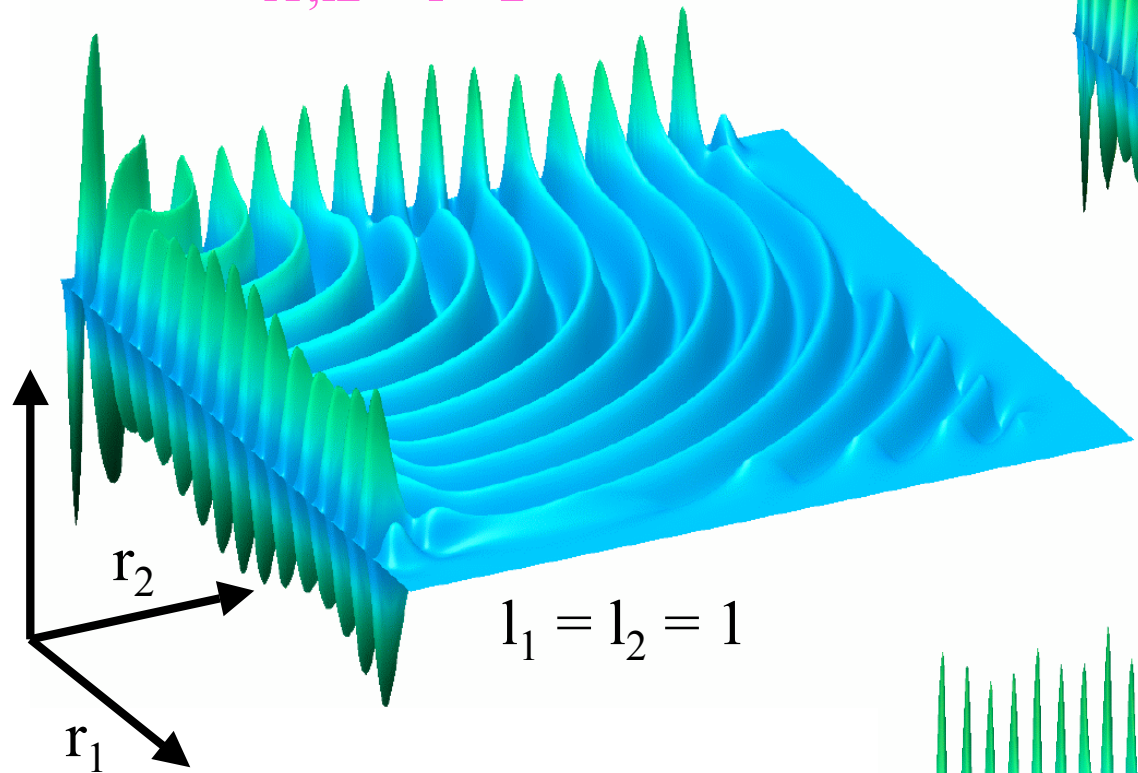
$\text{Re}[\Psi_{\text{SC}}(r_1, r_2)]$ for $e^- + \text{H} \rightarrow 2 e^- + p$



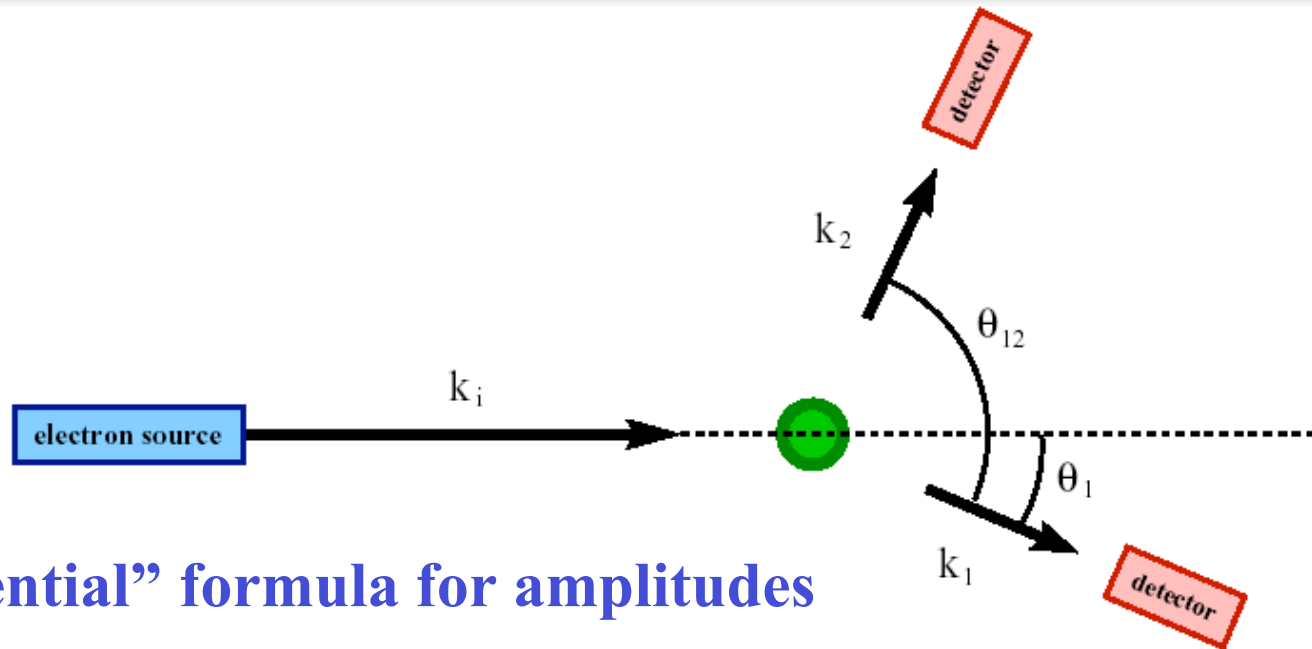
One component with
 $l_1 = l_2 = 1$

Wave Functions $e^- + H \rightarrow 2 e^- + p$

$$\text{Re}[\Psi_{11,12}^L(r_1, r_2)]$$



Extracting the Amplitudes and Cross Sections from the Wave Function



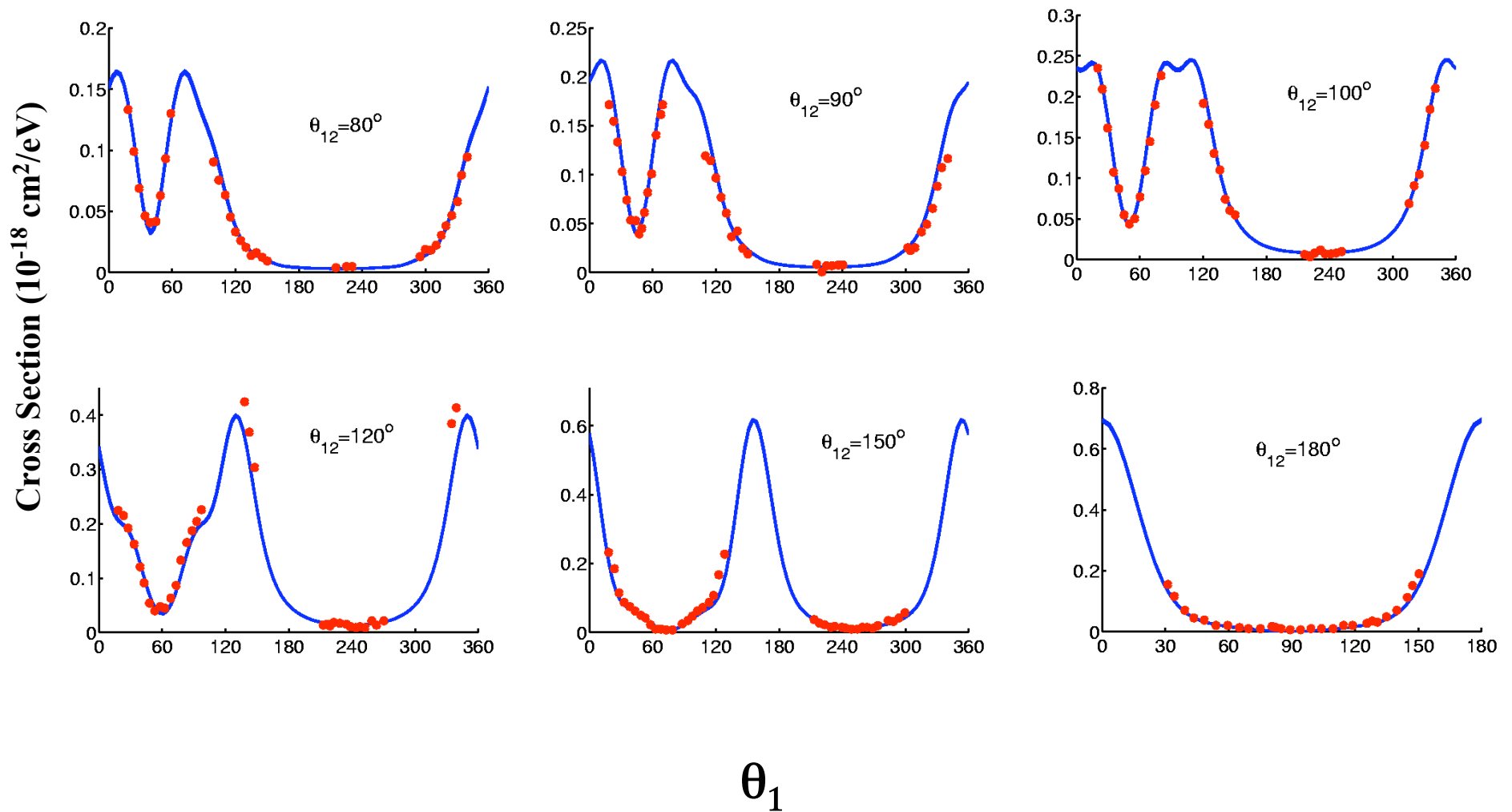
“Two potential” formula for amplitudes

$$f(\mathbf{k}_1, \mathbf{k}_2) = \left\langle \varphi_{\mathbf{k}_1}^{(-)} \varphi_{\mathbf{k}_2}^{(-)} \left| E - T + 1/r_1 + 1/r_2 \right| \Phi_{\text{sc}} \right\rangle$$

Surface integral form (*irrelevant overall volume dependent phase*)

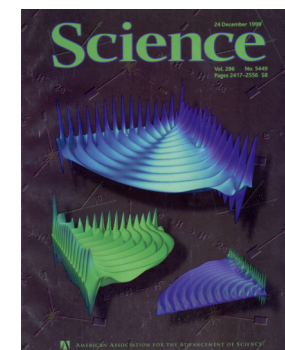
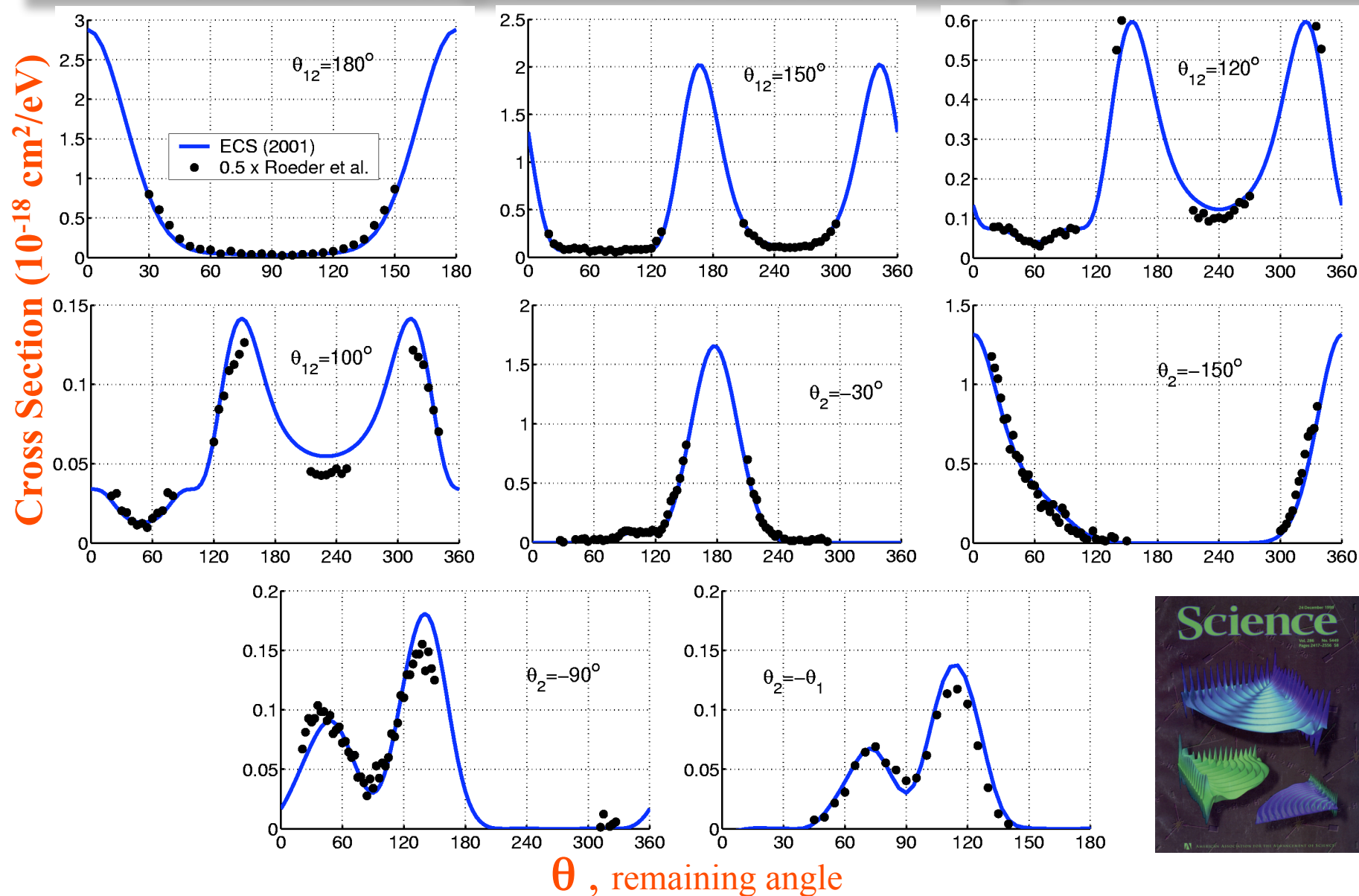
$$f(\mathbf{k}_1, \mathbf{k}_2) = \frac{1}{2} \int_S \left(\varphi_{\mathbf{k}_1}^{(-)} \varphi_{\mathbf{k}_2}^{(-)} \nabla \Phi_{\text{sc}} - \Phi_{\text{sc}} \nabla \varphi_{\mathbf{k}_1}^{(-)} \varphi_{\mathbf{k}_2}^{(-)} \right) \cdot \hat{n} dS$$

Triply Differential Cross Section -- Symmetric Coplanar 25 eV



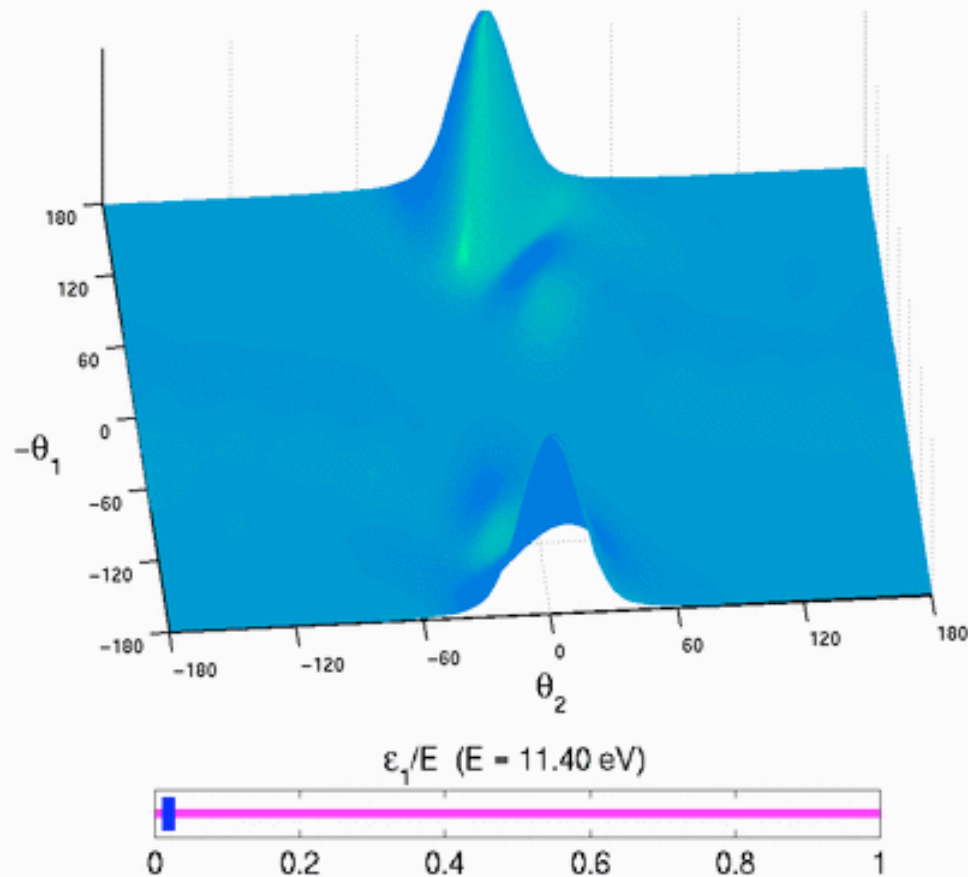
Experiment of Röder et. al

Triply Differential Cross Section at 15.6 eV, from surface integral – “reduced to computation”



$e^- + H$ Unequal Energy Sharing at 25 eV

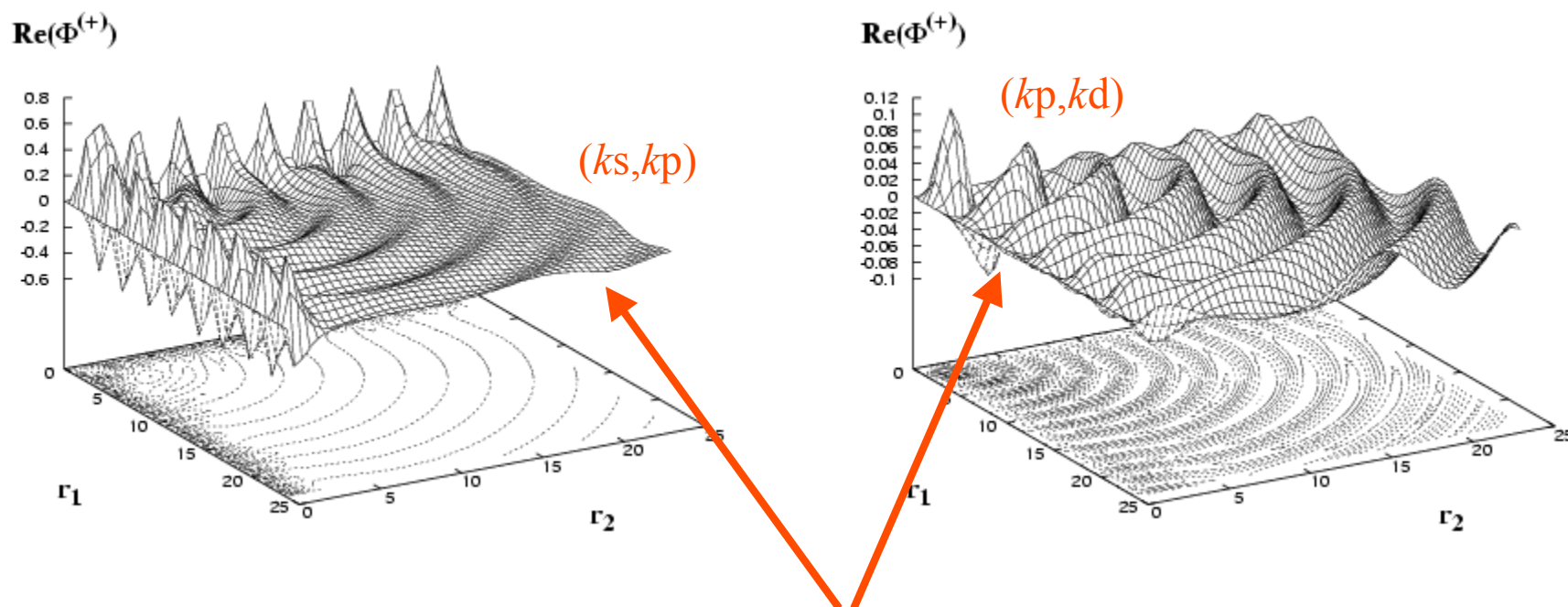
Triply
Differential
Cross
Section



Energy Sharing Fraction

Helium Double Photoionization Wavefunctions ($^1S \Rightarrow ^1P$ transitions)

Contributions of the continua (ks, kp) and (kp, kd) to $\text{Re}(\Phi^{(+)})$ for $h\nu=20\text{eV}$ above the double ionization threshold



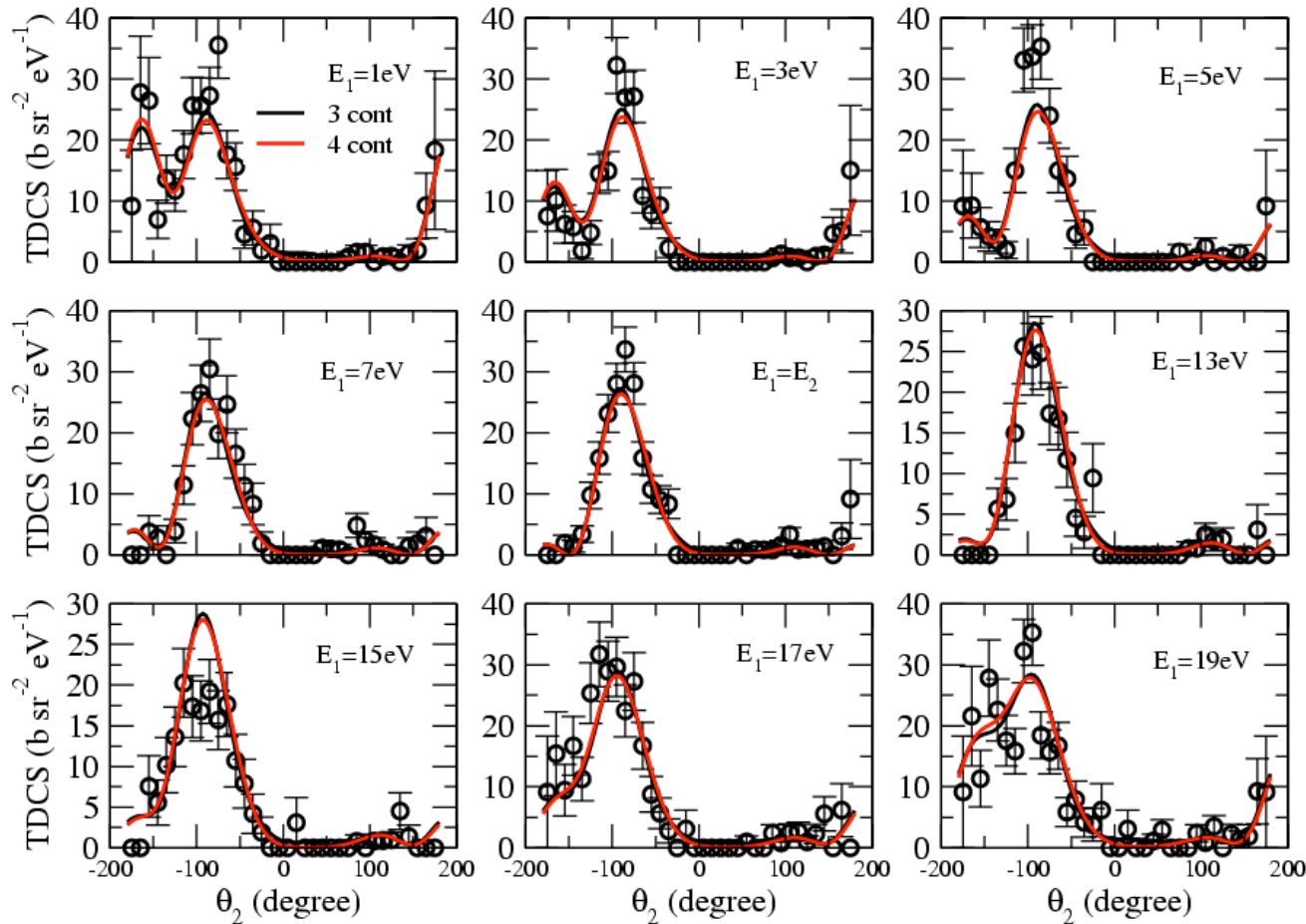
$$(E_0 + \hbar\omega - H)\Phi^{(+)} = \vec{\varepsilon} \cdot \vec{\mu} \Psi_0$$

Double ionization resides in the region of large r_1 and r_2
Single ionization resides in the regions where only one of r_1 or r_2 is large

Double Photoionization of Helium

4 continua (kskp, kpkd, kdkf, kfkf) 8100 config.

20eV above threshold, $R_0=29.23$ au, $\theta_{ECS}=30.0^\circ$, 46 bsplines, 45 basis functions; $\theta_1=30^\circ$



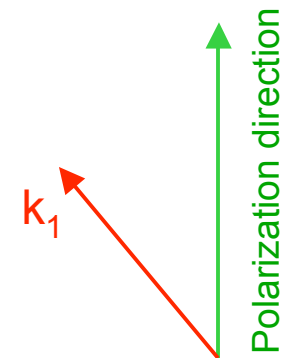
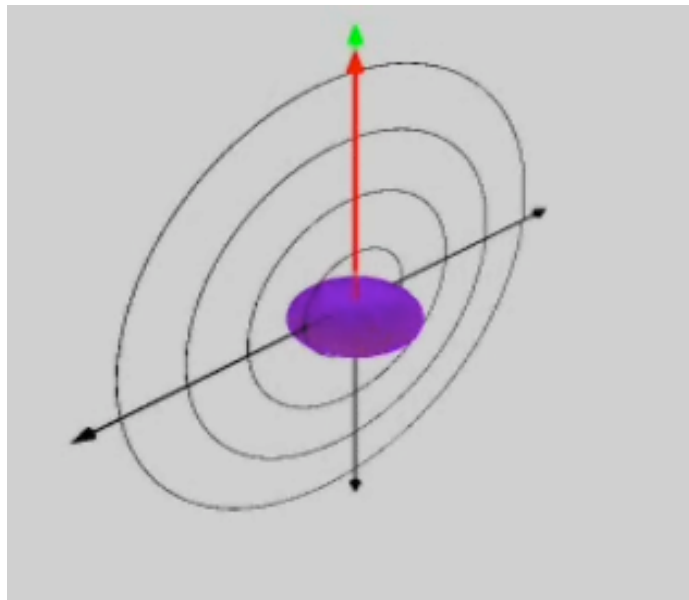
Exp: Brauning et al, J. Phys. B **31** 5149 (1998). Black line: kskp, kpkd and kdkf

Unequal energy sharing and $\theta_1 = 30^\circ$

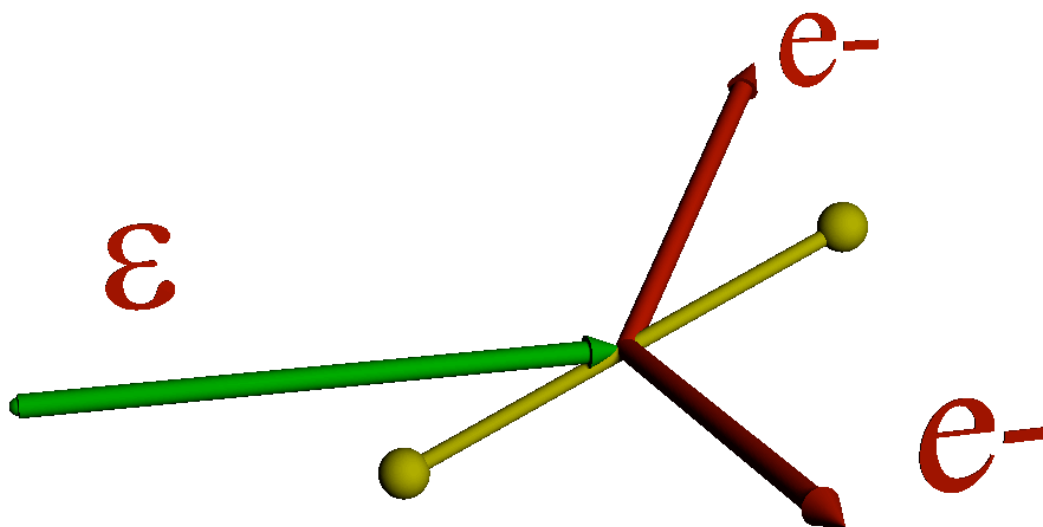
Double Photoionization of Helium

Triply Differential Cross Section for Equal Energy Sharing

20 eV excess photon energy

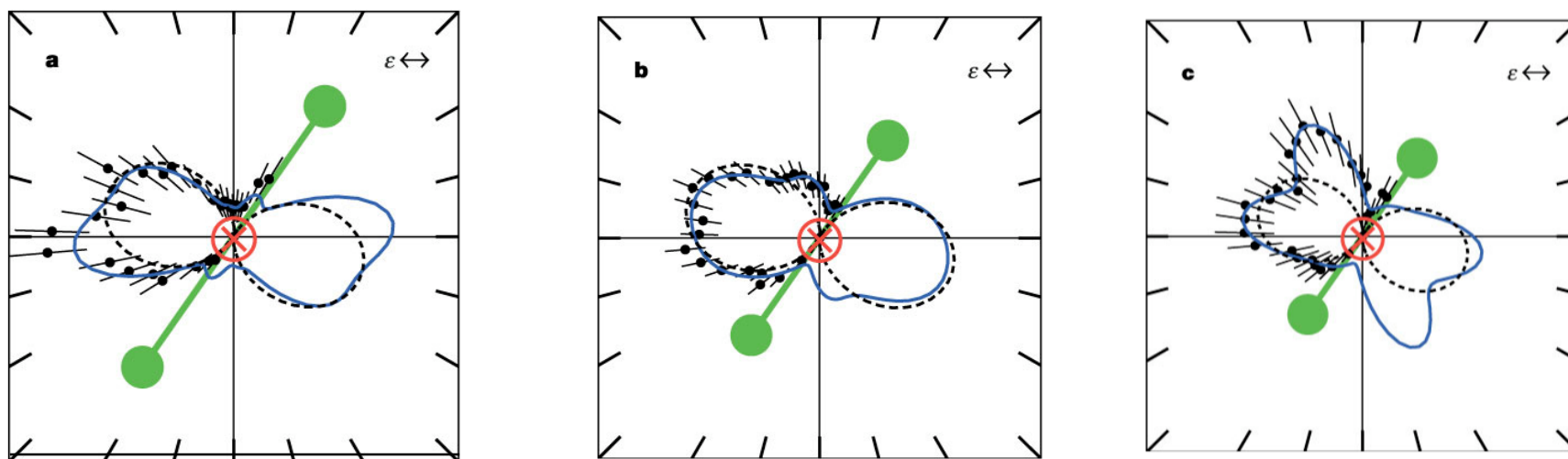


Molecular Double Photoionization: The Case of H_2



New COLTRIMS experiments at the ALS reveal *striking* molecular effects in the TDCS for *oriented* D_2

Angular Distributions with one electron coming towards you

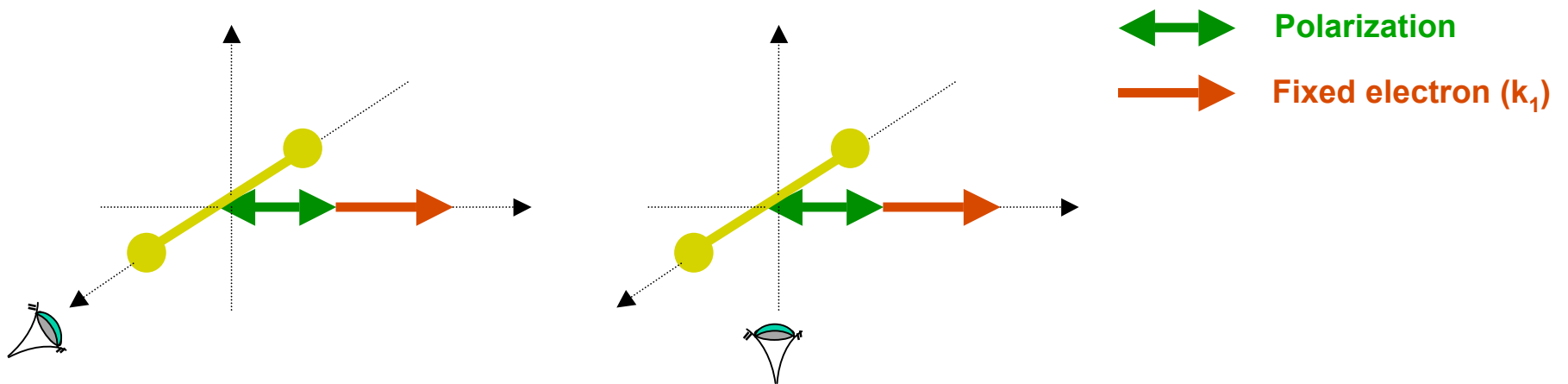


Varying Internuclear Distance

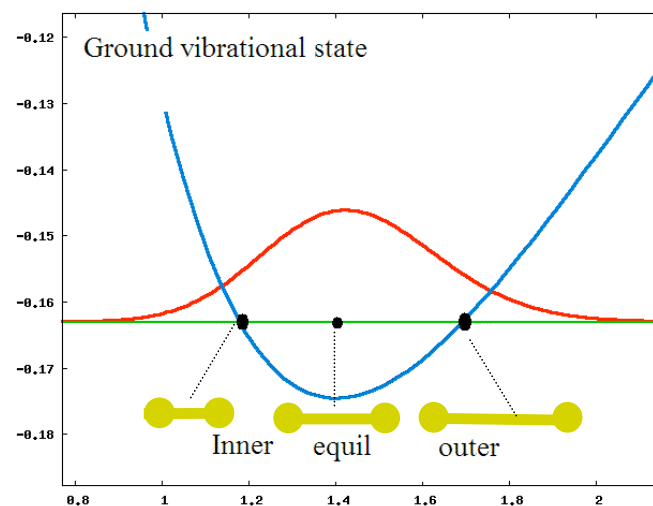
Th. Weber et al., Nature,
2004

Molecular correlation effects: H₂ vs. He

1. Changes in correlation due to the lower molecular symmetry



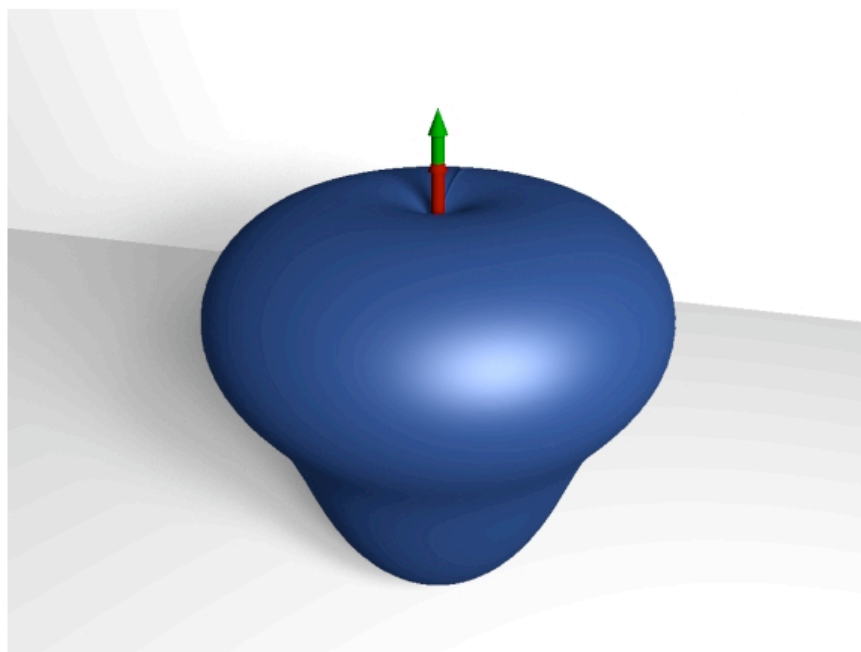
2. Changes in correlation due to variations in the internuclear distance



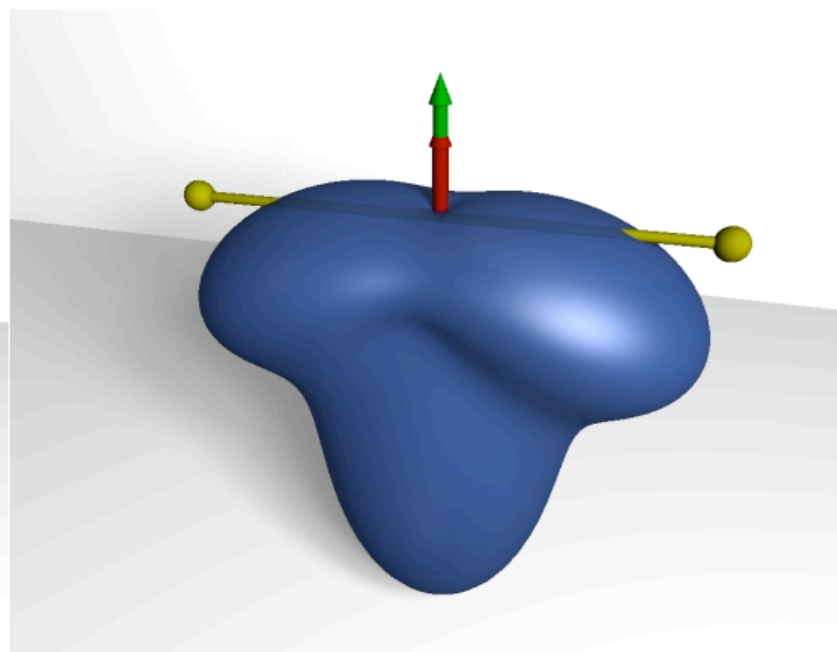
TDCS: changes in correlation due to molecular symmetry

90% energy sharing
24.5eV excess photon energy

↔ Polarization
→ Fixed electron (k_1)



He



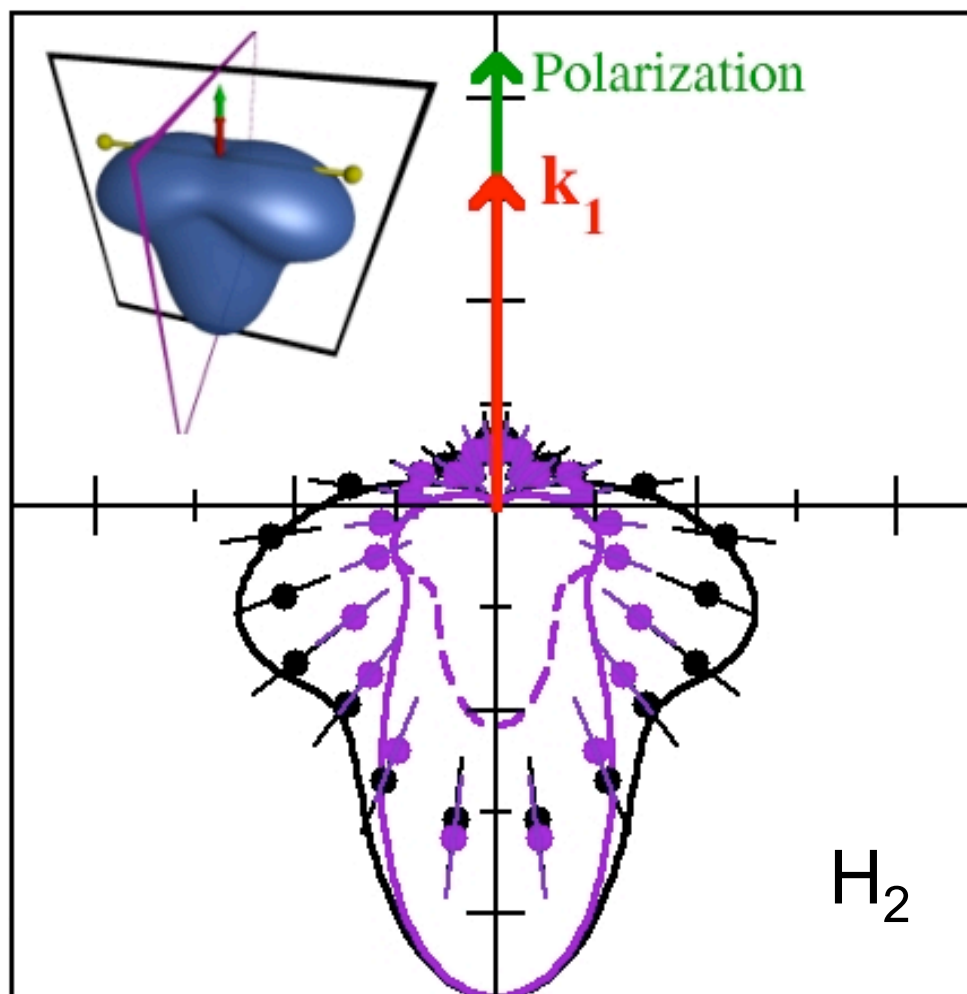
H₂

Vanroose, Martín, Rescigno and McCurdy
Science, 2005

TDCS: changes in correlation due to molecular symmetry

24.5eV excess photon energy

↔ Polarization
→ Fixed electron (k_1)





Energy sharing

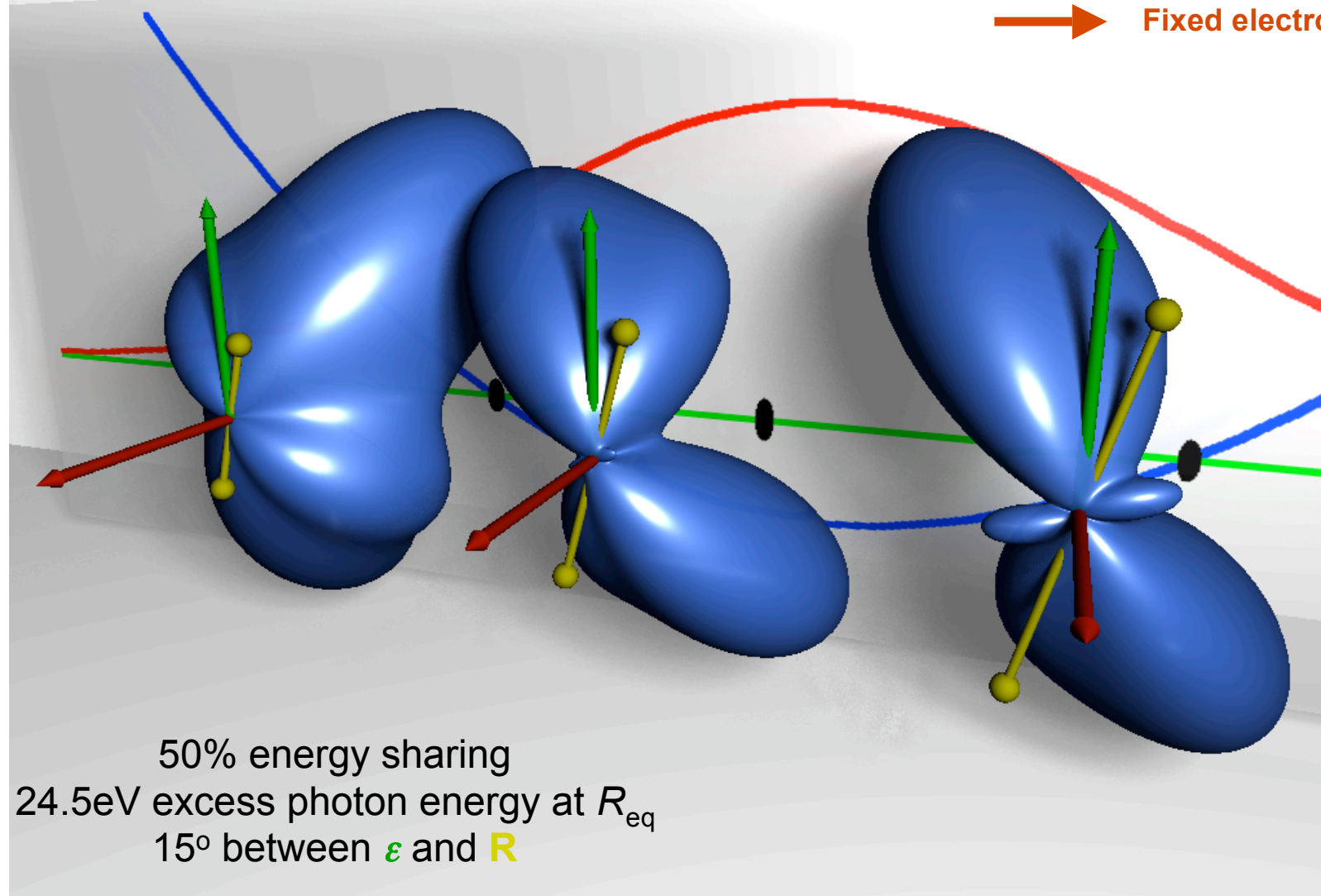
--- 80%

— 90%

TDCS: changes in correlation due to variations in R



Vanroose, Martín, Rescigno and McCurdy
Science (2005)

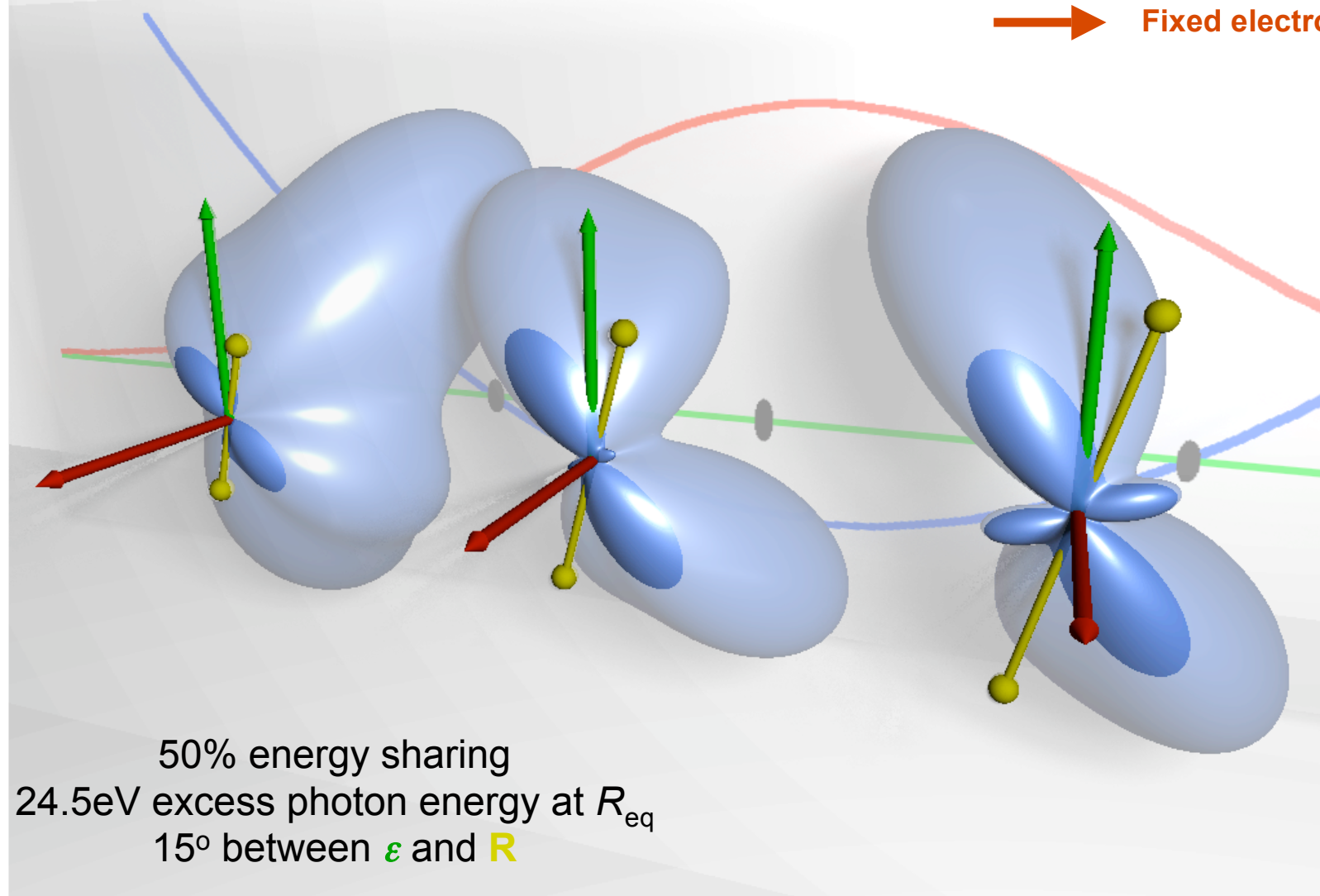
 Polarization
 Fixed electron (k_1)



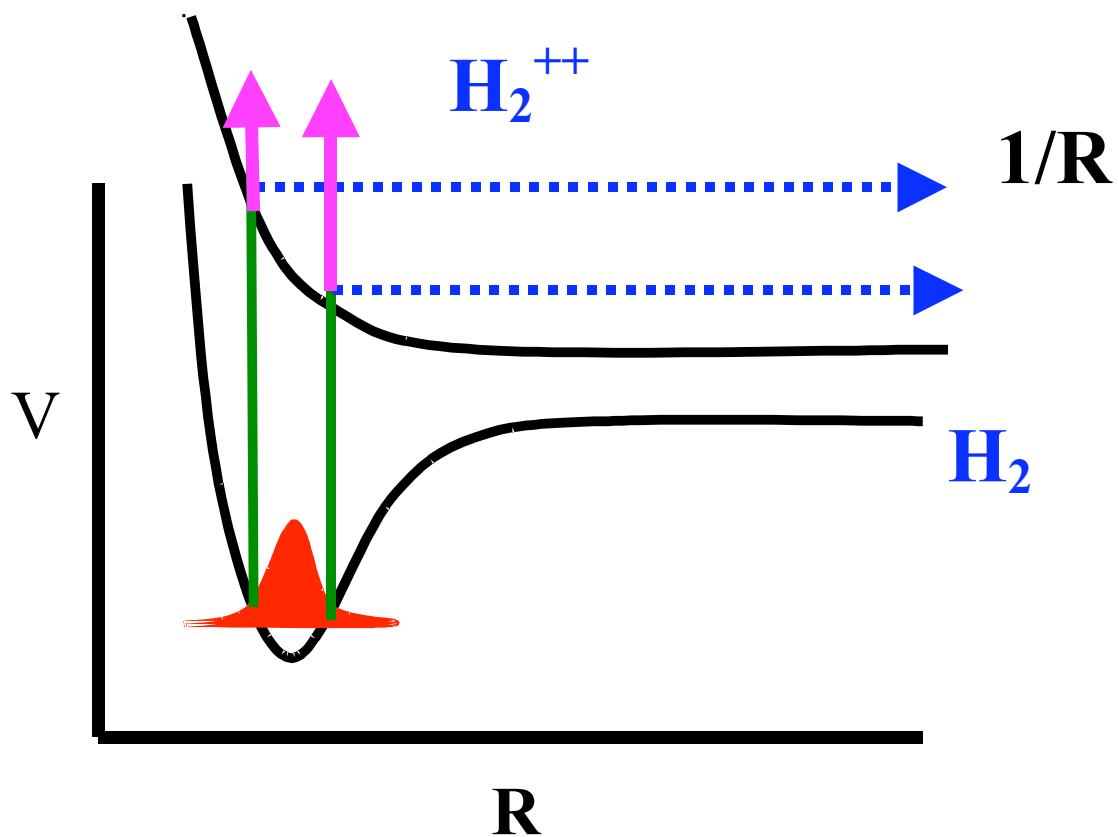
TDCS: changes in correlation due to variations in R

Vanroose, Martín, Rescigno and McCurdy
Science (2005)

 Polarization
 Fixed electron (k_1)





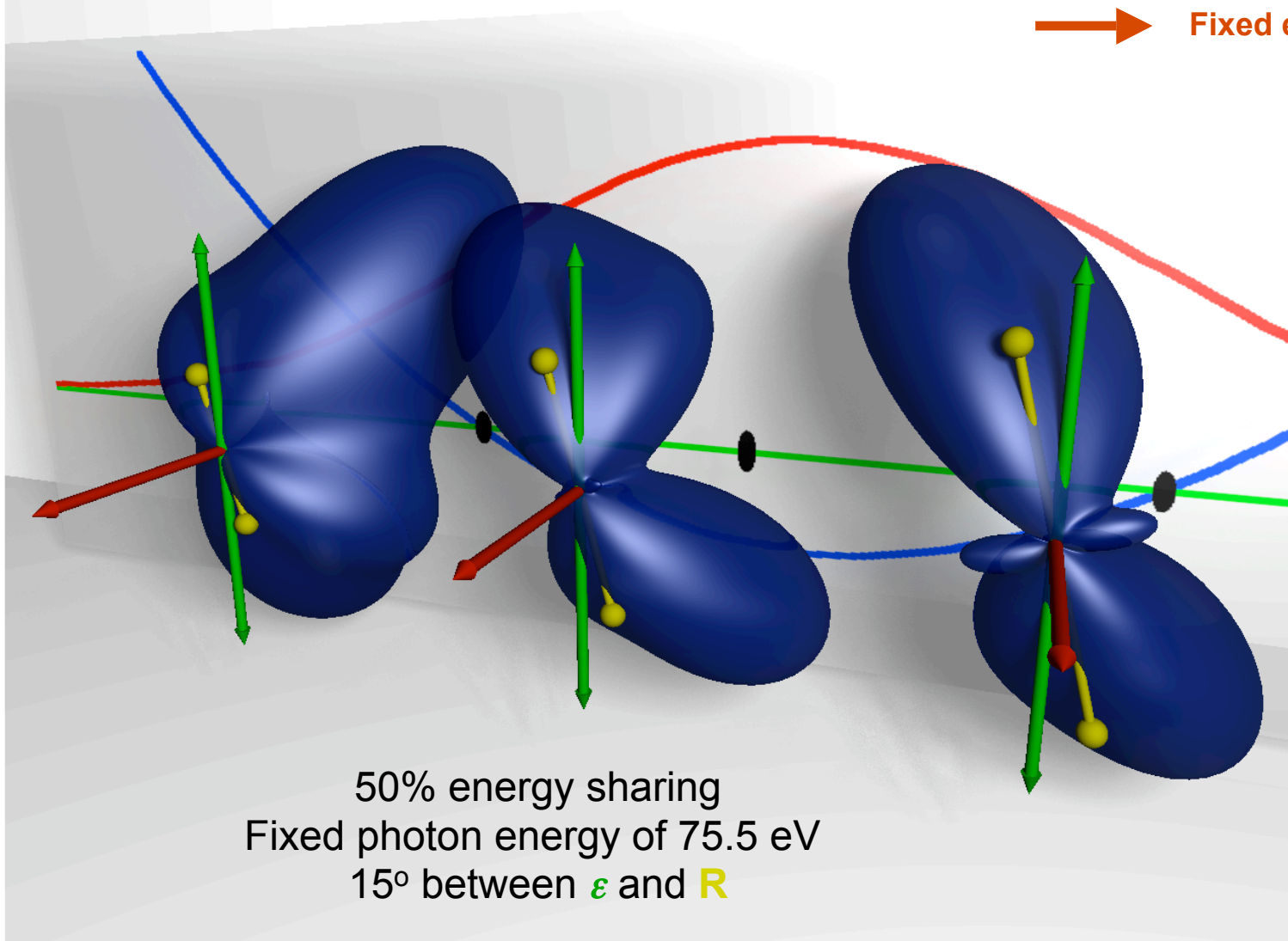
Wait a minute. Is this just a kinetic energy effect?



TDCS: changes in correlation due to variations in R



Vanroose, Martín, Rescigno and McCurdy
Science (2005)

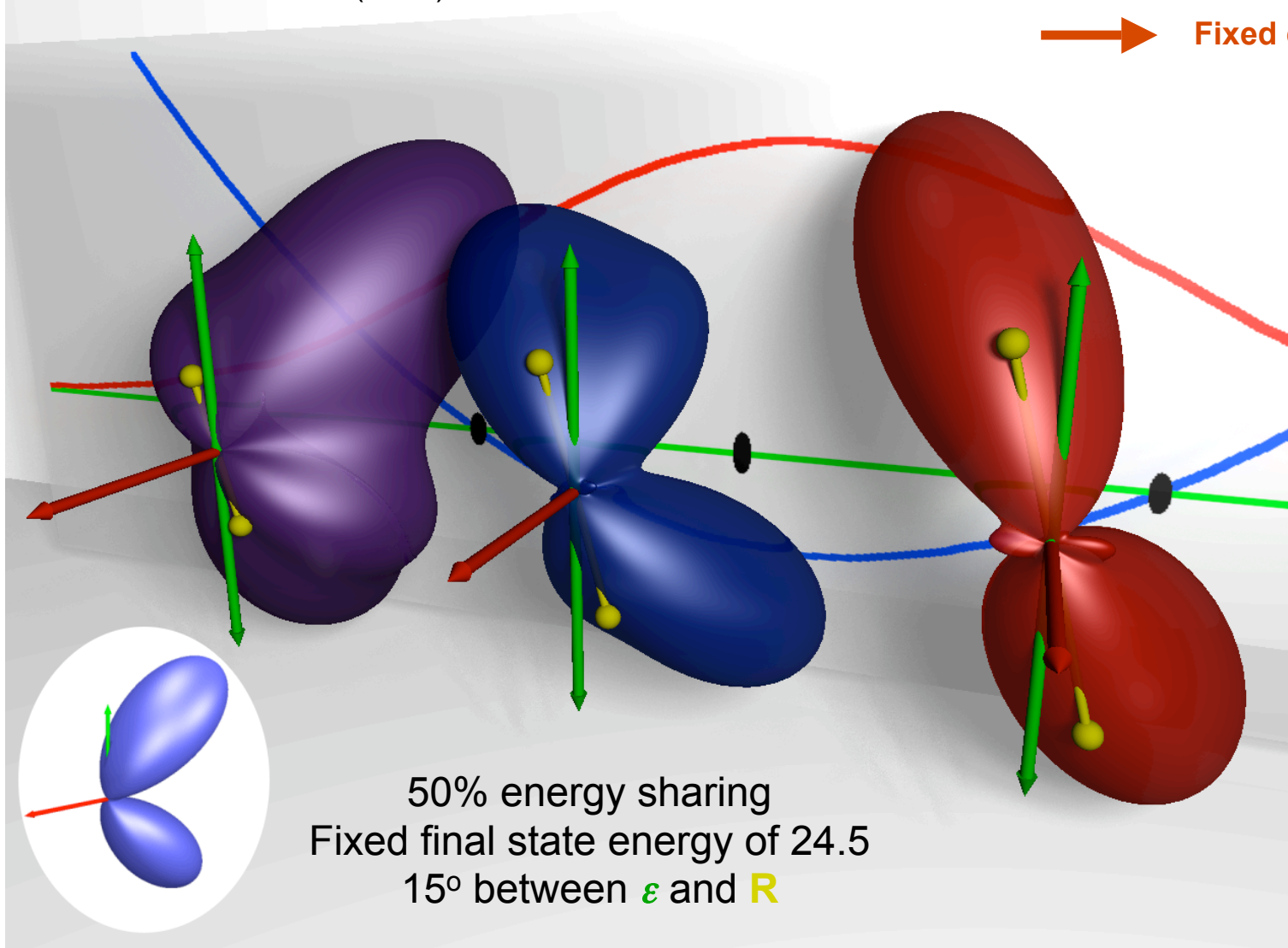
 Polarization
 Fixed electron (k_1)



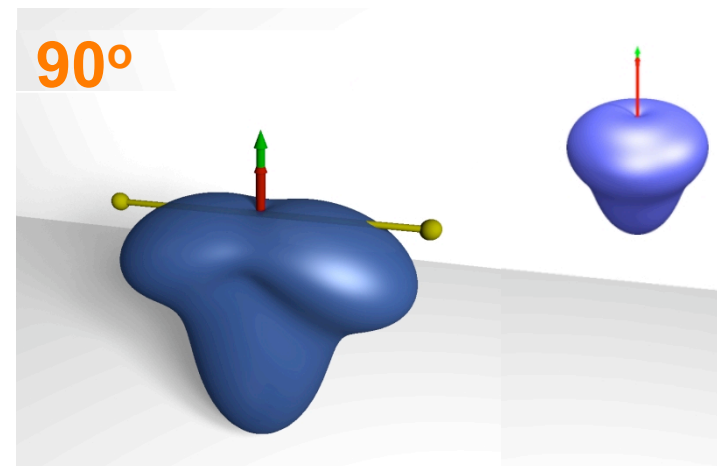
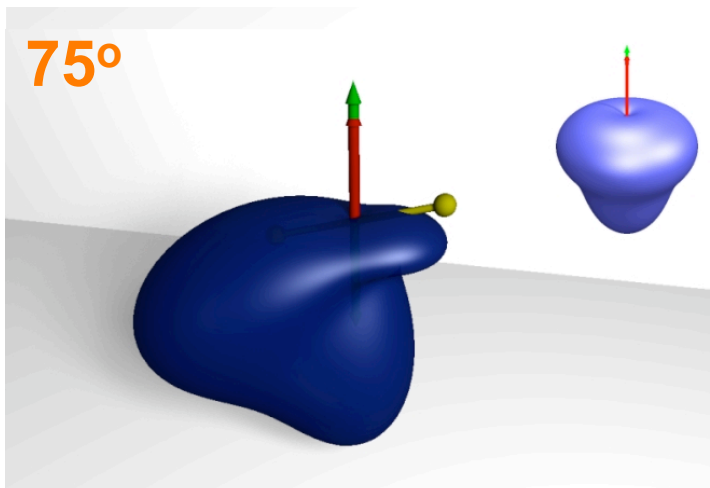
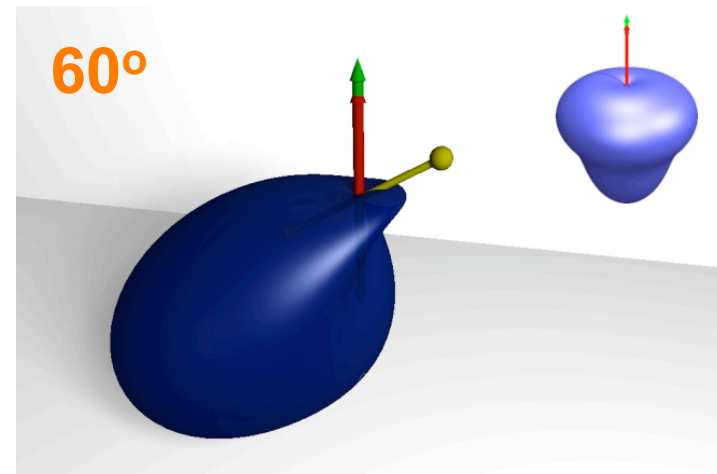
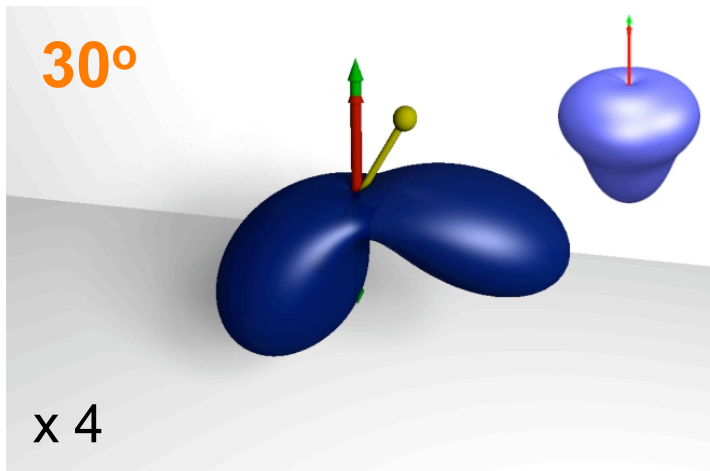
TDCS: changes in correlation due to variations in R

Vanroose, Martín, Rescigno and McCurdy
Science (2005)

 Polarization
 Fixed electron (k_1)



TDCS: probing different correlation for different orientations

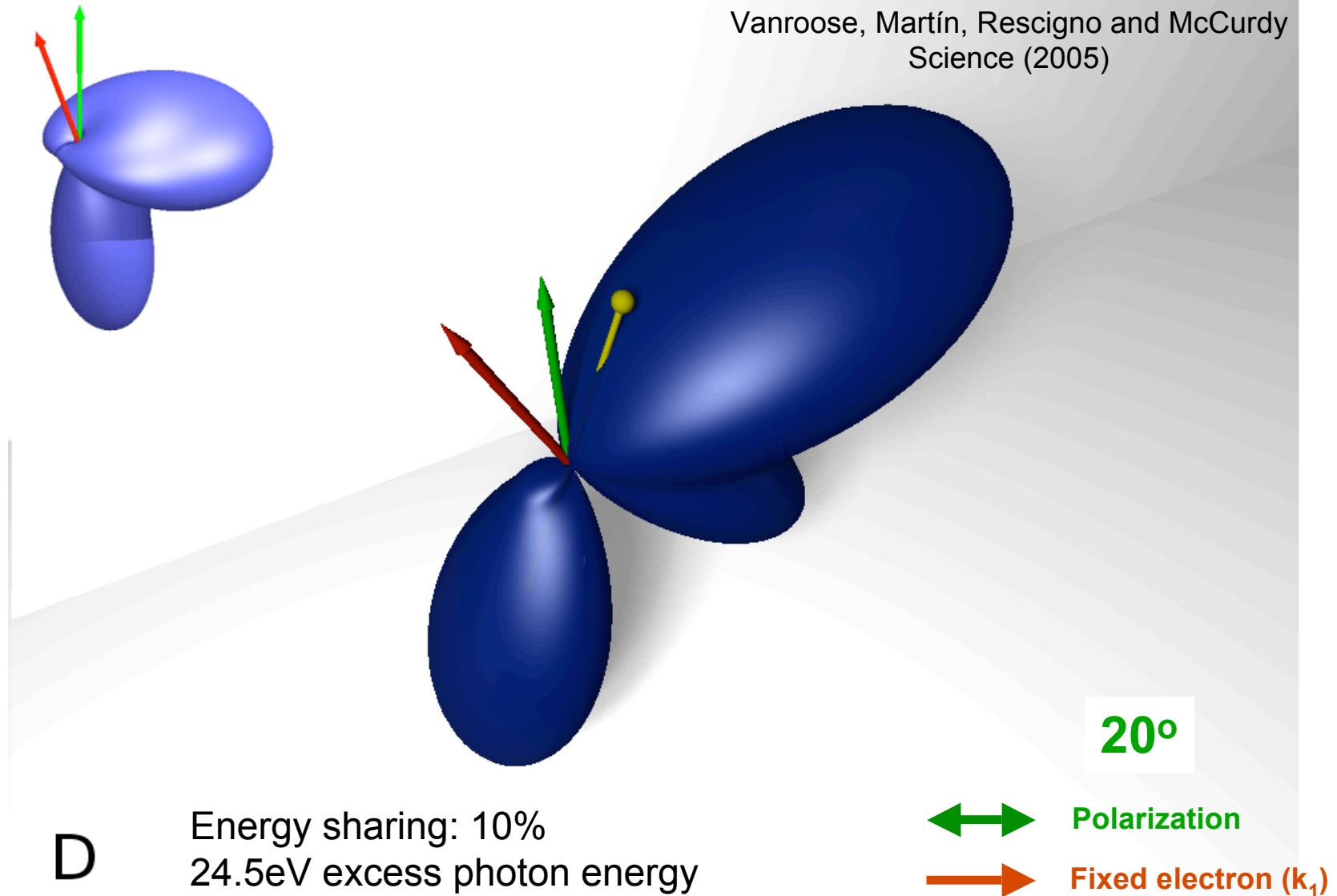


Energy sharing: 90%
24.5eV excess photon energy

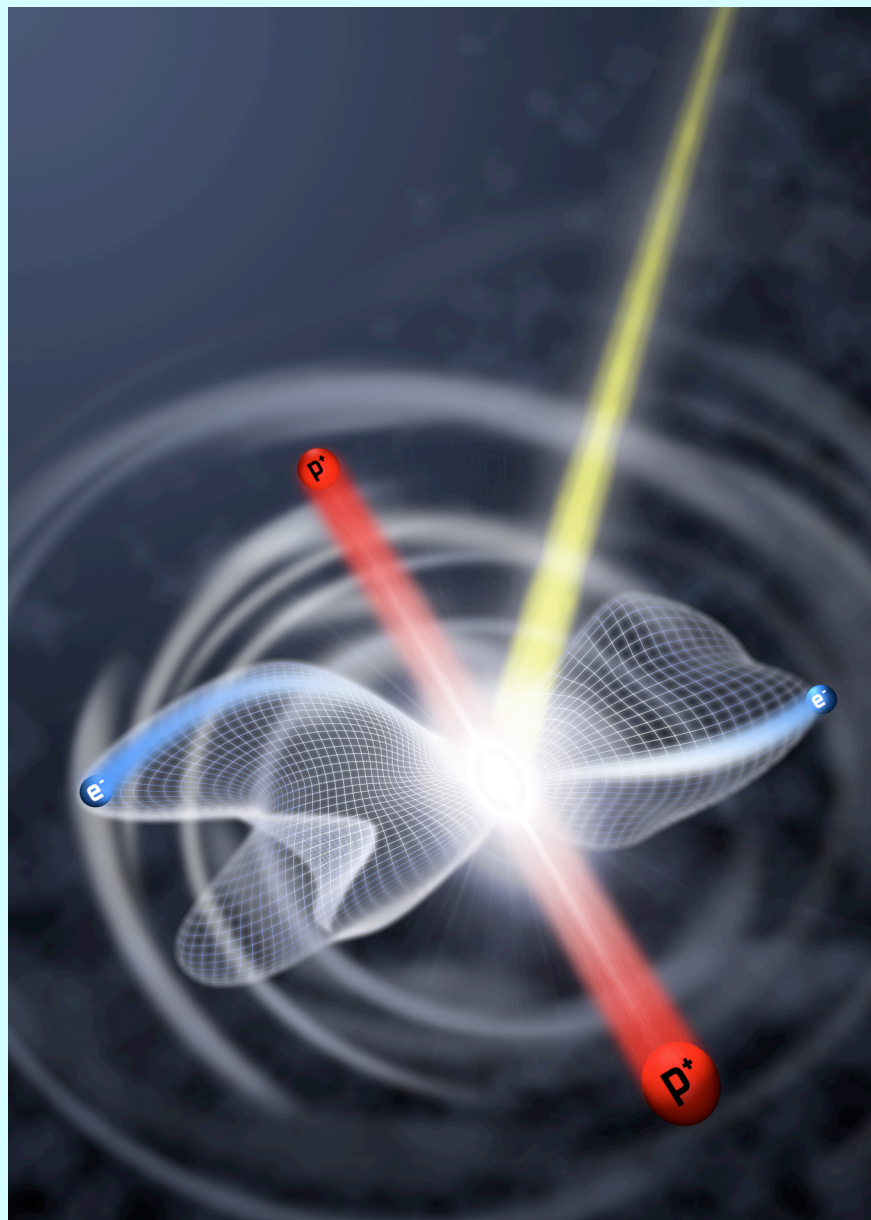
↔ Polarization
→ Fixed electron (k_1)

TDCS: probing different correlation for different orientations

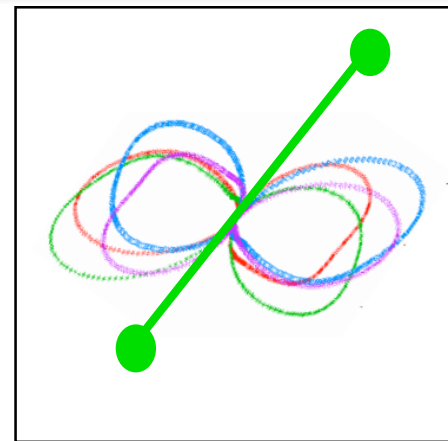
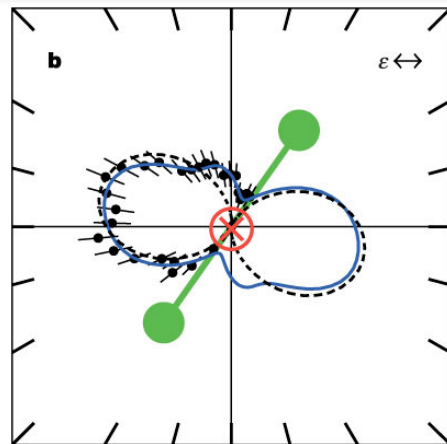
Vanroose, Martín, Rescigno and McCurdy
Science (2005)



A new spectroscopy? – probing electron correlation in a bond directly



Finite range of acceptance angles and energies dramatically affect the interpretation of the TDCS



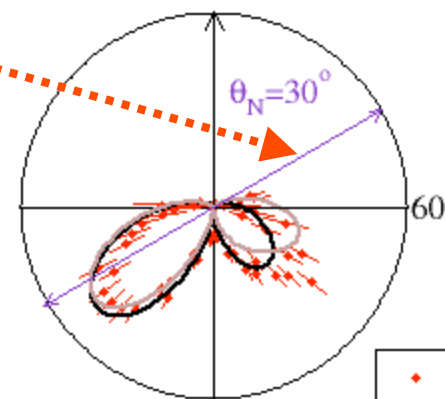
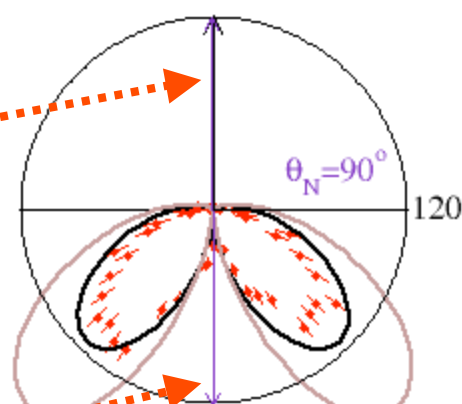
- Experiments have finite acceptance ranges for molecular orientation, electron direction and electron energy-sharing about nominal values.
- Broad acceptance ranges can obscure molecular effects
- Calculations can pinpoint specific effects and aid in interpreting experiments.

Integrating Over Acceptance Angles and Energy Resolution is Critical for Comparison with Experiments

- Experiments of Gisselbrect et al. PRL (2006) – absolute cross sections
- One electron perpendicular to polarization direction
- Angular resolutions $\pm 15^\circ$ to $\pm 20^\circ$ on electrons, and $\pm 20^\circ$ to $\pm 45^\circ$ on molecule
- Note that TDCS for “pure Σ orientation” with polarization along molecule is $\sim 1/10$ the TDCS for “pure Π ,” but acceptance angles mask that fact.

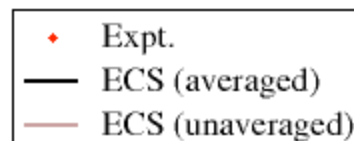
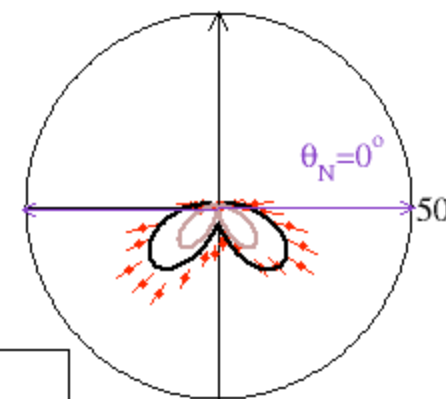
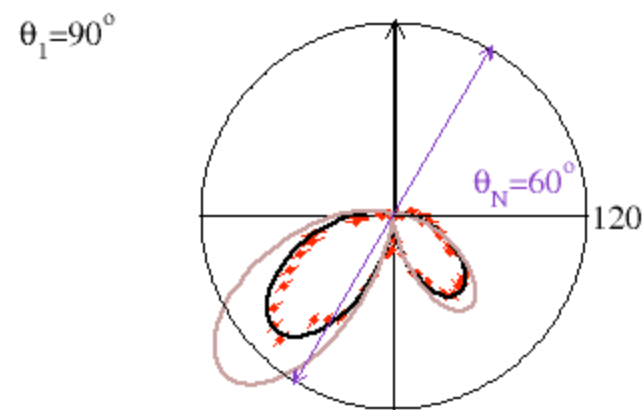
H₂ Double Photoionization

Differential Cross Sections



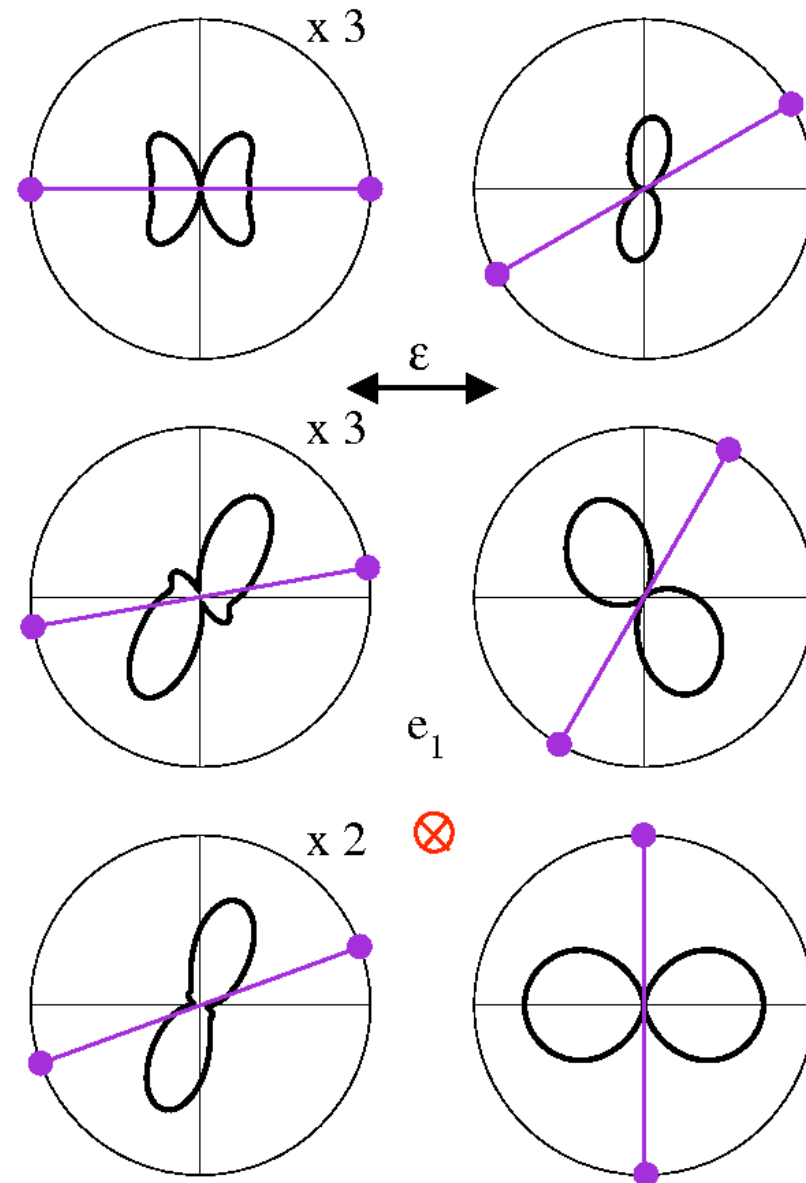
Equal Energy Sharing

$E_1 = E_2 = 12.5 \text{ eV} \pm 2.5 \text{ eV}$



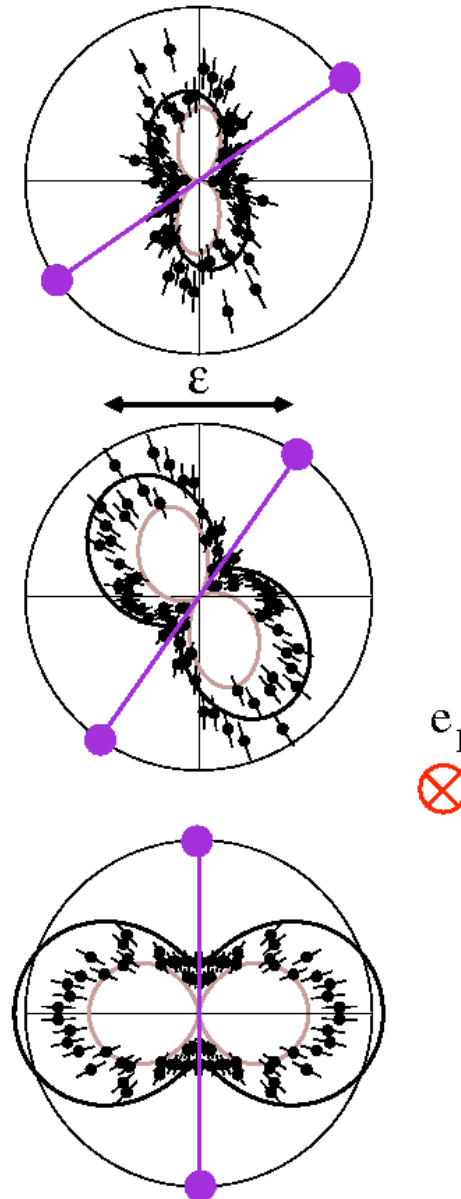
TDCS Rotating with Molecule

- Appears to rotate twice as fast as molecule! Reason is that pi contribution is ~ 7 times the sigma contribution



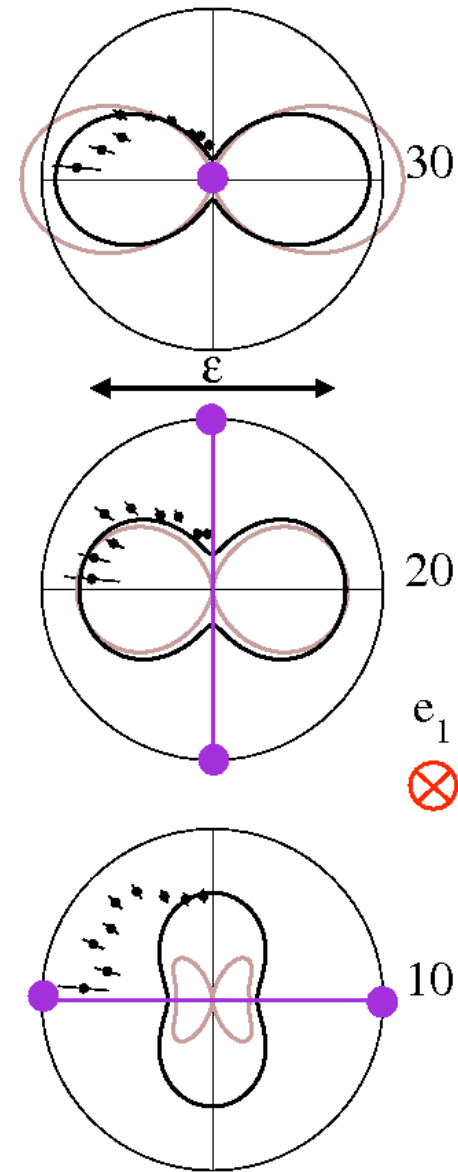
TDCS for Out of Plane Geometry

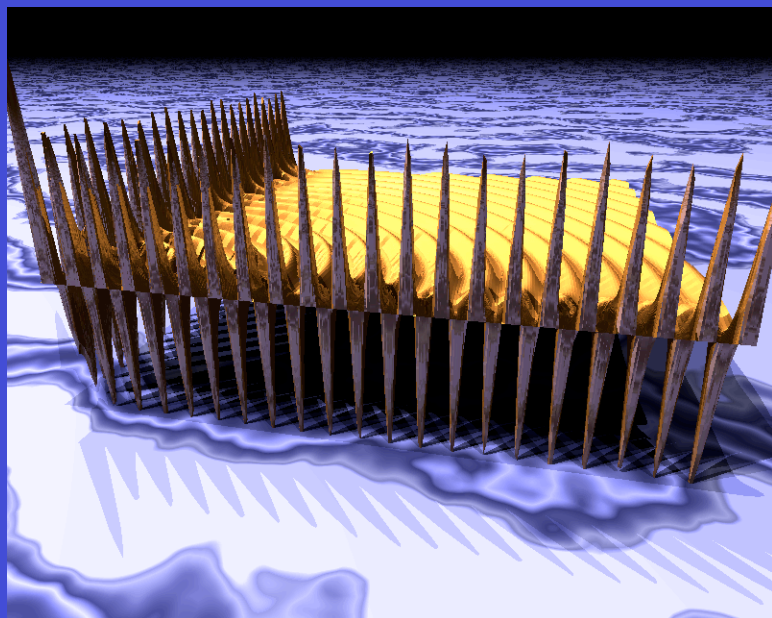
- Experiments of Weber et al. for equal energy sharing, with one electron coming out of the plane of the molecule and the polarization vector. Relative Cross Sections



Other Measurements of Out of Plane Geometry

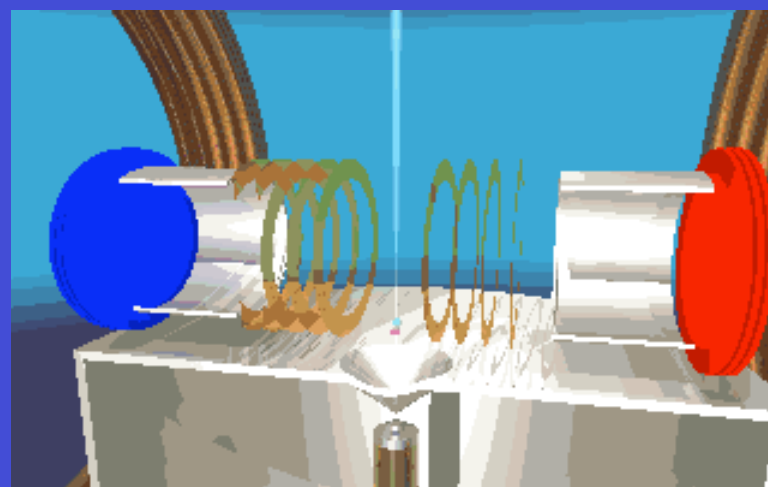
Experiments of Gisselbrecht, Huetz et al. PRL 2006





- Coulomb breakup problems for two electrons are now within the range of rigorous theory – using a combination of new formulations and high performance computing

- New experimental and theoretical techniques are opening the way to use these processes to study correlation in the chemical bond.





Dan Herner



Dan Haxton



Tom Rescigno

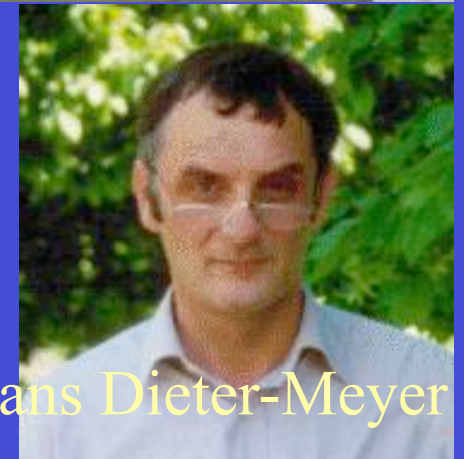


Wim Vanroose

Credits

“For excellence, the
presence of others is
required.”

Hannah Arendt, 1906-1975



Hans Dieter-Meyer



Cynthia Trevisan



Ann Orel



Frank Yin



Fernando Martin



Karel Houfek